

The Crystal Structures of the Rare Earth Pyrosilicates

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By means of X-ray diffraction, it has been established that four structure types occur in the rare earth pyrosilicates. They have the following symmetry: Sc, Yb, Tm silicates, $C2/m$; silicates of Er, Ho, Y, $P2_1/b$; those of Y, Ho, Dy, Gd, $Pna2_1$, and the rare earth silicates from Eu to La, $P2_12_12_1$. The crystal structures of $Yb_2Si_2O_7$ ($a=6.802$, $b=8.875$, $c=4.703$ Å; $\beta=102^\circ 07'$, $C2/m$, $Z=2$), $Er_2Si_2O_7$ ($a=4.683$, $b=5.556$, $c=10.79$ Å; $\gamma=96^\circ$, $P2_1/b$, $Z=2$), $Gd_2Si_2O_7$ ($a=13.87$, $b=5.073$, $c=8.33$ Å; $Pna2_1$, $Z=4$), $Nd_2Si_2O_7$ ($a=5.394$, $b=12.95$, $c=8.72$ Å; $P2_12_12_1$, $Z=4$) have been determined and refined by a least-squares method with the use of complete three-dimensional intensity data. Intensities were measured on a single-crystal diffractometer with a scintillation counter, using monochromatic Mo $K\alpha$ radiation. The final R values for these structures were 0.054, 0.062, 0.073 and 0.077 respectively. The atomic coordinates, bond lengths and valency angles are given. The simple π -bonding theory has been shown to be insufficient for describing the bond orders and bond lengths in the silicate anions of these compounds. The major factor responsible for the magnitude of these values appears to be the polarization effect of cations.

Introduction

An investigation of the structures of the rare earth silicates is of great interest in the crystal chemistry of silicates. These cations possess similar outer electron shells and therefore differ only very slightly in their chemical properties. The ionic radii of the rare earth elements increase monotonically from Lu to La.

The first investigations of the rare earth silicates were carried out by Giuscã (1934). In recent years these compounds were investigated by Warsaw & Roy (1964), who established on the basis of their X-ray powder patterns the existence of three structure types in the series of rare earth pyrosilicates and showed that pyrosilicates of the smallest rare-earth ions are isostructural with thortveitite. No crystallographic data were obtained because the rare earth silicates had not been synthesized in single-crystal form.

Preliminary X-ray studies have enabled us to establish four structure types in the rare earth series of increasing cation size from Sc to La. The crystal structures of the Yb, Er, Gd and Nd pyrosilicates belonging to different structure types are described here. Finally, the results obtained are reviewed, and some questions of the chemical bonding in these compounds are discussed.

Experimental

The $Ln_2Si_2O_7$ compounds (where $Ln=La, Ce, Nd, Sm, Eu, Gd, Dy, Ho, Y, Er, Tm$ and Yb) were obtained by sintering the oxides in the ratio $Ln_2O_3:2SiO_2$ at 1500° (Toropov, Bondar & Calachov, 1962). X-ray powder patterns showed that the rare earth pyrosilicates form four structurally separate types of compound. The first type (according to increasing ionic radii of the cations) contains the Sc, Yb, Tm and probably Lu pyrosilicates. The second type includes the pyrosilicates of Er, Ho and Y. The Y, Ho, Dy and

Gd ions form the third type of 1:2 compound. The Ho and Y pyrosilicates prepared by sintering the oxides at $1300^\circ C$ are isostructural with $Er_2Si_2O_7$ and transform into the third structure type at a temperature above $1500^\circ C$. The remaining rare earth ions from Eu through La yield the fourth type of pyrosilicate.

Further investigations of these compounds were carried out on single crystals of $Yb_2Si_2O_7$, $Er_2Si_2O_7$, $Gd_2Si_2O_7$ and $Nd_2Si_2O_7$ grown by the Verneuil method. The cell dimensions and space groups of these crystals were determined from rotation and equi-inclination Weissenberg photographs. The cell dimensions were further refined using a single-crystal diffractometer. The cell dimensions of the other compounds were determined from their indexed X-ray powder patterns.

Complete data in three dimensions were obtained on a single-crystal diffractometer with monochromatic Mo $K\alpha$ radiation and a scintillation counter using the moving-crystal stationary-counter technique. The normal-beam method was employed for measurements of intensities. Background corrections were obtained from a plot of intensity *versus* angle made with the crystal out of the reflecting position. The intensities of all reflexions with $\sin \theta/\lambda \leq 1.1$ Å⁻¹ were measured in every layer. The crystals were ground to effectively polished spherical shapes (from 0.24 to 0.32 mm in diameter) (Smolin & Shepelev, 1968a). In no case did the diameter of the spheroids used deviate from that of the equivalent sphere by more than 0.02 mm. Absorption corrections as described in *International Tables for X-ray Crystallography* (1959) were applied to all reflexions. The intensity data were also corrected for the usual Lorentz and polarization factors.

The crystal structure of $Yb_2Si_2O_7$

The investigation of the $Yb_2Si_2O_7$ single crystal confirmed that it is isostructural with thortveitite: the unit

cell is monoclinic, and the possible space groups are $C2/m$, $C2$ and Cm . The cell dimensions of $Yb_2Si_2O_7$ and $Tm_2Si_2O_7$ together with those of $Sc_2Si_2O_7$ (Cruickshank, Lynton & Barclay, 1962) are listed in Table 1.

The density determined with a pycnometer was 5.99 g.cm^{-3} , compared with 6.15 g.cm^{-3} predicted for two formula units per unit cell. Intensity data for six layers around the c axis (hkl with $l=0$ to 5, 1220 reflexions) were collected.

After considering the three possible space groups mentioned above, Cruickshank, Lynton & Barclay (1962) concluded that the correct one for $Sc_2Si_2O_7$ was $C2/m$, thus supporting Zachariasen's (1930) conclusion that the Si-O-Si angle in the pyrosilicate group is 180° . Because the substitution of Sc for Yb, which differs significantly in size, could reduce the crystal symmetry, the structure of $Yb_2Si_2O_7$ was refined by a three-dimensional least-squares method with isotropic thermal vibrations for all atoms in each of the space groups $C2/m$, $C2$ and Cm . The structure-factor least-squares program of Tarnopolsky & Andrianov (1964) was used here and subsequently.

The initial trial structure was based upon the structure of $Sc_2Si_2O_7$. The scattering factors were taken from Cromer & Waber (1965) with a dispersion correction for Yb, and the weighting scheme used was:

$$w = 1/(a + F_o + bF_o^2)$$

where $a = 2F_{\min}$, $b = 2/F_{\max}$ (Cruickshank, Pilling, Bujosa, Lovell & Truter, 1961).

The final R values obtained were 0.054 for group $C2/m$ and 0.053 for space groups $C2$ and Cm . The analysis of the distances and configuration of the pyrosilicate ion enabled us to exclude the space group Cm owing to the unreasonable variation in the Si-O

bond lengths (from 1.567 to 1.683 Å) and in the tetrahedral angles (from $100^\circ 100' 2''$ to $114^\circ 24'$). The variation is less for space group $C2$: 0.03 Å in the Si-O bond lengths, and about 6° in the tetrahedral angles. For space group $C2/m$, the Si-O distances and tetrahedral angles differed by up to 0.018 Å and $5^\circ 46'$ respectively. The Si-O-Si angle is $174 \pm 1^\circ$ for Cm , $176 \pm 1^\circ$ for $C2$ and 180° for $C2/m$. Space group $C2$ gave $B = 1.7 \text{ Å}^2$ for the bridge oxygen atom, which is a very high value for rare earth silicates, and a large difference (almost twice as high as for $C2/m$) between the temperature factors of the chemically equivalent oxygen atoms O(2) and O(3). The space group $C2$ was therefore also excluded and the space group $C2/m$ was considered to be the correct one for $Yb_2Si_2O_7$.

Taking this into account, the space group $C2/m$ has to be considered as correct for $Yb_2Si_2O_7$. $Yb_2Si_2O_7$ is thus fully isostructural with $Sc_2Si_2O_7$, and the Si-O-Si bond in its pyrosilicate group is linear. In Table 2 are listed the results of the least-squares refinement of the $Yb_2Si_2O_7$ structure in space group $C2/m$.

The structure of $Yb_2Si_2O_7$ is shown in Fig. 1. The numbers represent the approximate heights of atoms expressed in hundredths of the c axis. The Yb octahedron is strongly distorted and has symmetry 2. Each Yb ion is coordinated to six oxygen atoms at distances Yb-O(2), 2.218; Yb-O(3), 2.209; Yb-O(3'), 2.284 Å (all $\pm 0.004 \text{ Å}$). The bond lengths and valence angles in the pyrosilicate group are given in Table 3.

The mean Si-O terminal bond length is 1.626 Å.

The crystal structure of $Er_2Si_2O_7$

The $Er_2Si_2O_7$ crystal is monoclinic and the systematic absences indicated the space group $P2_1/b$ uniquely. The

Table 1. Cell dimensions of $Sc_2Si_2O_7$, $Yb_2Si_2O_7$ and $Tm_2Si_2O_7$

	a	b	c	β
$Sc_2Si_2O_7$	$6.542 \pm 0.005 \text{ Å}$	$8.519 \pm 0.005 \text{ Å}$	$4.669 \pm 0.005 \text{ Å}$	$102^\circ 33 \pm 10'$
$Yb_2Si_2O_7$	6.802 ± 0.005	8.875 ± 0.01	4.703 ± 0.005	$102^\circ 07 \pm 10'$
$Tm_2Si_2O_7$	6.824 ± 0.01	8.91 ± 0.01	4.704 ± 0.005	$101^\circ 50 \pm 10'$

Table 2. Atomic coordinates with estimated standard deviations (e.s.d.'s) and isotropic temperature factors for $Yb_2Si_2O_7$

	x/a	$\sigma(x/a)$	y/b	$\sigma(y/b)$	z/c	$\sigma(z/c)$	B
Yb	$\frac{1}{2}$	—	0.80687	0.00002	0	—	0.25 Å^2
Si	0.7189	0.0003	$\frac{1}{2}$	—	0.4125	0.0006	0.37
O(1)	$\frac{1}{2}$	—	$\frac{1}{2}$	—	$\frac{1}{2}$	—	1.02
O(2)	0.8831	0.0005	$\frac{1}{2}$	—	0.7151	0.0015	0.50
O(3)	0.7361	0.0005	0.6504	0.0004	0.2197	0.0011	0.54

Table 3. Bond lengths with e.s.d.'s and valence angles in the pyrosilicate group

Si-O(1)	$1.626 \pm 0.003 \text{ Å}$	O(1)-O(2)	$2.590 \pm 0.004 \text{ Å}$	O(1)-Si-O(2)	$106^\circ 07'$
Si-O(2)	1.614 ± 0.006	O(1)-O(3)	2.643 ± 0.004	O(1)-Si-O(3)	$108^\circ 28'$
Si-O(3)	1.632 ± 0.005	O(2)-O(3)	2.689 ± 0.007	O(2)-Si-O(3)	$111^\circ 53'$
		O(3)-O(3')	2.670 ± 0.007	O(3)-Si-O(3')	$109^\circ 49'$
				Si—O(1)-Si	180°

unit-cell dimensions of $\text{Er}_2\text{Si}_2\text{O}_7$ and $\text{Ho}_2\text{Si}_2\text{O}_7$ are given in Table 4, together with those for $\text{Y}_2\text{Si}_2\text{O}_7$ quoted by Batulieva, Bondar, Sidorenko & Toropov (1967).

The cell contains two formula units. The calculated density is 5.98 g.cm^{-3} , and the observed value 5.85 g.cm^{-3} .

The crystal structure of $\text{Er}_2\text{Si}_2\text{O}_7$ was determined with 1860 hkl amplitudes (Smolin & Shepelev, 1968*b*). Intensity data were collected for layers $hk0$ – $hk11$ around the c axis. By using the three-dimensional Patterson function, the erbium atom was located. The heavy-atom technique was used to locate the silicon and oxygen atoms. A further three-dimensional least-squares refinement reduced the R value to 0.062. The

scattering factors for Er, Si and O were taken from *International Tables for X-ray Crystallography* (1962). The erbium scattering factor was corrected for dispersion. The weighting scheme of Hughes was used. The structure of $\text{Er}_2\text{Si}_2\text{O}_7$ is shown in Fig. 2. The approximate values of the x coordinates for atoms are given, as well as the environment for the cations. The final results of the refinement are listed in Table 5.

A striking feature of the $\text{Er}_2\text{Si}_2\text{O}_7$ structure is that centrosymmetry of the Si_2O_7 group follows directly from the space group $P2_1/b$ indicated uniquely by the systematic absences. Fourfold general positions and twofold special positions (on the centres of symmetry) are possible in this space group. Since the unit cell contains only two pyrosilicate groups, they necessarily

Table 4. Cell dimensions of $\text{Er}_2\text{Si}_2\text{O}_7$, $\text{Y}_2\text{Si}_2\text{O}_7$ and $\text{Ho}_2\text{Si}_2\text{O}_7$

	a	b	c	γ
$\text{Er}_2\text{Si}_2\text{O}_7$	$4.683 \pm 0.005 \text{ \AA}$	$5.556 \pm 0.005 \text{ \AA}$	$10.79 \pm 0.01 \text{ \AA}$	$96^\circ \pm 10'$
$\text{Y}_2\text{Si}_2\text{O}_7$	4.663 ± 0.005	5.536 ± 0.005	10.784 ± 0.021	$96^\circ 06'$
$\text{Ho}_2\text{Si}_2\text{O}_7$	4.686 ± 0.005	5.58 ± 0.005	10.84 ± 0.02	$95^\circ 58 \pm 10'$

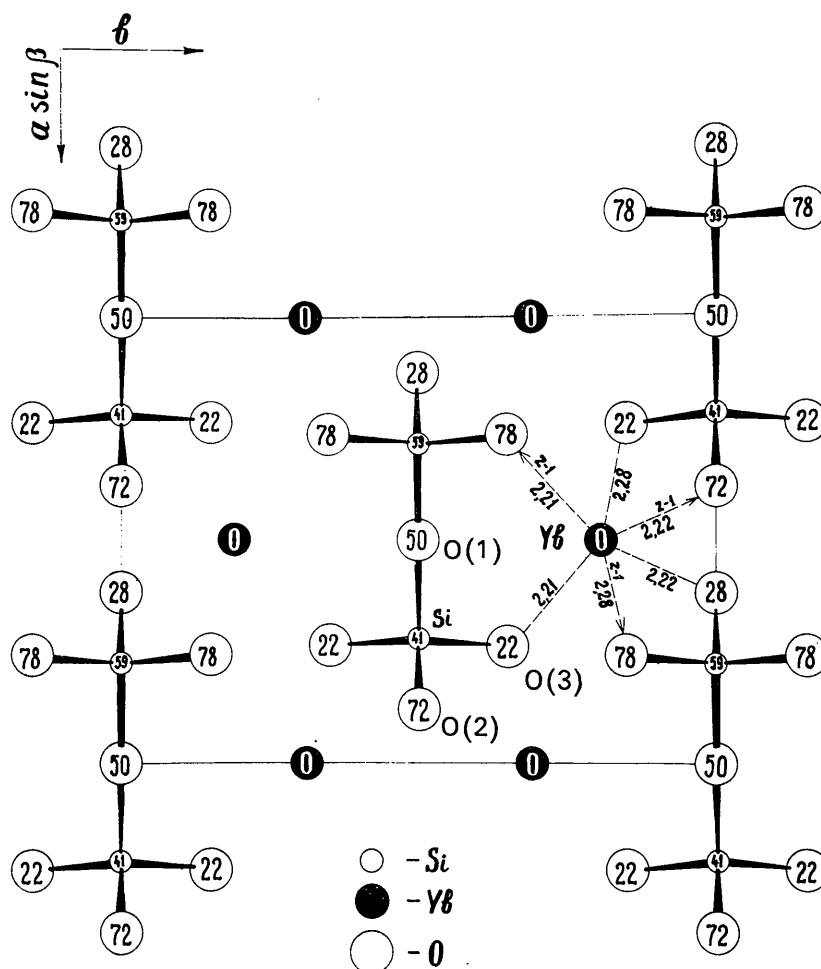


Fig. 1. The structure of $\text{Yb}_2\text{Si}_2\text{O}_7$ projected along the c axis.

occupy these special positions. Evidence for the linearity of the Si-O-Si bond does not therefore depend on considerations arising only during the structure refinement, as was the case with $\text{Sc}_2\text{Si}_2\text{O}_7$ and $\text{Yb}_2\text{Si}_2\text{O}_7$. Thus, the structure of $\text{Er}_2\text{Si}_2\text{O}_7$ appears to provide further evidence for the possibility of the existence of Si_2O_7 groups with a Si-O-Si angle equal to 180° . The bond lengths and valence angles in the pyrosilicate group are given in Table 6.

The mean Si-O terminal bond length is 1.617 \AA . The terminal oxygen atoms of the pyrosilicate group form strongly distorted octahedra around the erbium atoms similar to those around the ytterbium atom in $\text{Yb}_2\text{Si}_2\text{O}_7$. The bridging oxygen atom O(1) is not bonded to an erbium atom. Oxygen atoms of one polyhedron (Fig. 2) belong to different pyrosilicate groups. Each octahedron is pointed to three other octahedra by common edges O(2)-O(2') (2.79 \AA),

Table 5. Atomic coordinates with e.s.d.'s and isotropic temperature factors for $\text{Er}_2\text{Si}_2\text{O}_7$

	x/a	$\sigma(x/a)$	y/b	$\sigma(y/b)$	z/c	$\sigma(z/c)$	B
Er	0.88829	0.00008	0.09318	0.00006	0.34934	0.00005	0.29 \AA^2
Si	0.3601	0.0004	0.6442	0.0003	0.3871	0.0003	0.33
O(1)	$\frac{1}{2}$	—	$\frac{1}{2}$	—	$\frac{1}{2}$	—	0.91
O(2)	0.2052	0.0008	0.8653	0.0007	0.4486	0.0006	0.64
O(3)	0.1235	0.0009	0.4583	0.0008	0.3191	0.0006	0.63
O(4)	0.6184	0.0009	0.7522	0.0007	0.2984	0.0006	0.56

Table 6. Bond lengths with e.s.d.'s and valence angles

Si-O(1)	$1.632 \pm 0.003 \text{ \AA}$	O(1)-O(2)	$2.630 \pm 0.004 \text{ \AA}$	O(1)-Si-O(2)	$107^\circ 24'$
Si-O(2)	1.631 ± 0.005	O(1)-O(3)	2.625 ± 0.006	O(1)-Si-O(3)	$108^\circ 03'$
Si-O(3)	1.611 ± 0.005	O(1)-O(4)	2.615 ± 0.006	O(1)-Si-O(4)	$107^\circ 36'$
Si-O(4)	1.609 ± 0.005	O(2)-O(3)	2.652 ± 0.007	O(2)-Si-O(3)	$109^\circ 44'$
		O(2)-O(4)	2.649 ± 0.008	O(2)-Si-O(4)	$109^\circ 43'$
		O(3)-O(4)	2.701 ± 0.006	O(3)-Si-O(4)	$114^\circ 03'$
				Si-O(1)-Si	180°

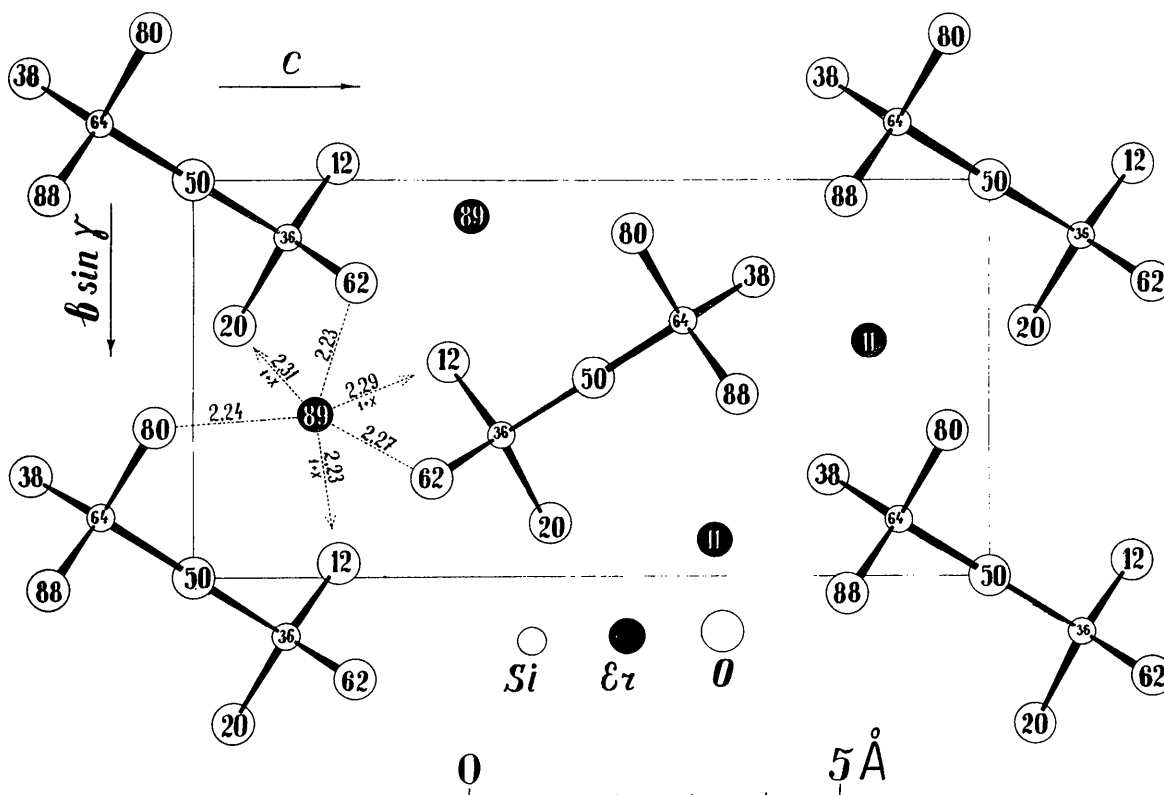


Fig. 2. The structure of $\text{Er}_2\text{Si}_2\text{O}_7$ projected along the a axis.

O(3)–O(4) (twice) (2.82 Å). Interatomic Er–O distances are given in Table 7.

The crystal structure of Gd₂Si₂O₇

The Gd₂Si₂O₇ crystal is orthorhombic with $Z=4$ ($D_m=5.33$, $D_c=5.46$ g.cm⁻³). The space group deduced from absent reflexions is either *Pnam* or *Pna2₁*. A new structure refinement shows the space group to be *Pna2₁*. The cell dimensions for pyrosilicates of this structure type are given in Table 8.

The crystal structure of Gd₂Si₂O₇ was determined by three-dimensional Patterson and difference Fourier syntheses (Smolin & Shepelev, 1967). Intensity data were collected for layers 0–5 around the *b* axis and zone *hk0* (about 1300 reflexions). The approximate atomic coordinates obtained from Patterson and Fourier syntheses were satisfactory for the space group *Pnam*. However, a three-dimensional least-squares refinement of Gd₂Si₂O₇ reduced the *R* value only to 0.167 with unreasonable variations in the Si–O bond lengths

within the pyrosilicate group. The symmetry of the space group *Pnam* was therefore assumed to be valid only to a first approximation. The least-squares refinement of the structure was carried out in the non-centrosymmetric space group *Pna2₁*. The scattering factors for Gd, Si and O taken from *International Tables for X-ray Crystallography* (1962) and the Hughes weighting scheme were used. The final *R* value was reduced to 0.073 with a much smaller variation in the Si–O bond lengths. Consequently, one ought to regard the space group *Pna2₁* as correct for Gd₂Si₂O₇ and for pyrosilicates isostructural with it. The results of the refinement are listed in Table 9.

The structure of Gd₂Si₂O₇ is shown in Fig. 3. Each of the Gd atoms is coordinated by seven oxygen atoms. Coordination polyhedra of gadolinium ions are formed by both the terminal and the bridge oxygen atoms. The Gd–O distances are given in Table 10.

Apart from O(4), which is bonded to two silicon atoms and two gadolinium ions, each oxygen atom, as well as being bonded to a silicon atom, is also coordi-

Table 7. Er–O interatomic distances with *e.s.d.*'s

Er–O(2)	2.312 ± 0.005 Å	Er–O(2')	2.240 ± 0.007 Å
Er–O(3)	2.229 ± 0.005	Er–O(3')	2.290 ± 0.006
Er–O(4)	2.233 ± 0.005	Er–O(4')	2.270 ± 0.006

Table 8. Cell dimensions of Y₂Si₂O₇, Ho₂Si₂O₇, Dy₂Si₂O₇ and Gd₂Si₂O₇

	<i>a</i>	<i>b</i>	<i>c</i>
Y ₂ Si ₂ O ₇	13.69 ± 0.02 Å	5.02 ± 0.005 Å	8.165 ± 0.01 Å
Ho ₂ Si ₂ O ₇	13.70 ± 0.015	4.98 ± 0.005	8.23 ± 0.01
Dy ₂ Si ₂ O ₇	13.74 ± 0.015	5.012 ± 0.005	8.26 ± 0.01
Gd ₂ Si ₂ O ₇	13.87 ± 0.015	5.073 ± 0.005	8.33 ± 0.01

Table 9. Atomic coordinates with *e.s.d.*'s and isotropic temperature factors for Gd₂Si₂O₇

	<i>x/a</i>	$\sigma(x/a)$	<i>y/b</i>	$\sigma(y/b)$	<i>z/c</i>	$\sigma(z/c)$	<i>B</i>
Gd(1)	0.12551	0.00004	0.33730	0.00013	0.99831	0.00007	0.38 Å ²
Gd(2)	0.12564	0.00004	0.33739	0.00013	0.51409	0.00007	0.36
Si(1)	0.3205	0.0002	0.3744	0.0007	0.2505	0.0009	0.31
Si(2)	0.5390	0.0002	0.6253	0.0006	0.2498	0.0008	0.17
O(1)	0.2715	0.0007	0.4769	0.0022	0.0876	0.0013	0.58
O(2)	0.2658	0.0006	0.4857	0.0021	0.4130	0.0012	0.34
O(3)	0.3457	0.0006	0.0706	0.0017	0.2465	0.0015	0.44
O(4)	0.4211	0.0005	0.5557	0.0016	0.2448	0.0011	0.23
O(5)	0.5472	0.0008	0.7858	0.0023	0.0866	0.0014	0.61
O(6)	0.5456	0.0008	0.7882	0.0025	0.4206	0.0015	0.73
O(7)	0.5988	0.0005	0.3526	0.0017	0.2560	0.0019	0.60

Table 10. Gd–O interatomic distances with *e.s.d.*'s

Gd(1)–O(1)	2.270 ± 0.010 Å	Gd(1)–O(5)	2.319 ± 0.011 Å
Gd(1)–O(2)	2.441 ± 0.010	Gd(1)–O(6)	2.473 ± 0.012
Gd(1)–O(3)	2.441 ± 0.012	Gd(1)–O(7)	2.381 ± 0.015
Gd(1)–O(4)	2.630 ± 0.009		
Gd(2)–O(1)	2.399 ± 0.011 Å	Gd(2)–O(5)	2.485 ± 0.011 Å
Gd(2)–O(2)	2.248 ± 0.009	Gd(2)–O(6)	2.334 ± 0.012
Gd(2)–O(3)	2.303 ± 0.012	Gd(2)–O(7)	2.386 ± 0.015
Gd(2)–O(4)	2.481 ± 0.009		

nated to two Gd ions. Pauling's valence rule is consequently unsatisfied. The pyrosilicate group occupies a general position in the $Gd_2Si_2O_7$ structure. The Si-O-Si angle is $158^\circ 40' \pm 40'$. The bond lengths and angles within the pyrosilicate group are given in Table 11.

The mean Si-O terminal distance is 1.614 \AA for the given structure. The shortest edges of the tetrahedra [O(2)-O(4), 2.594 ; O(1)-O(4), 2.486 ; O(4)-O(5), 2.481 ;

O(4)-O(6), 2.553 \AA] are shared with the Gd poly-dra.

The crystal structure of $Nd_2Si_2O_7$

$Nd_2Si_2O_7$ is orthorhombic, with space group $P2_12_12_1$; $Z=4$; $D_m=5.04$, $D_c=4.98 \text{ g.cm}^{-3}$. The cell dimensions of $Nd_2Si_2O_7$ and silicates isostructural with it are given in Table 12.

Table 11. Bond lengths with e.s.d.'s and valence angles in the Si_2O_7 group

Si(1)-O(1)	$1.604 \pm 0.013 \text{ \AA}$	O(1)-O(2)	$2.712 \pm 0.015 \text{ \AA}$	O(1)-Si(1)-O(2)	$112^\circ 50'$
Si(1)-O(2)	1.651 ± 0.012	O(1)-O(3)	2.657 ± 0.015	O(1)-Si(1)-O(3)	$113^\circ 05'$
Si(1)-O(3)	1.581 ± 0.009	O(1)-O(4)	2.486 ± 0.013	O(1)-Si(1)-O(4)	$98^\circ 40'$
Si(1)-O(4)	1.672 ± 0.008	O(2)-O(3)	2.754 ± 0.014	O(2)-Si(1)-O(3)	$116^\circ 53'$
		O(2)-O(4)	2.594 ± 0.012	O(2)-Si(1)-O(4)	$102^\circ 37'$
		O(3)-O(4)	2.674 ± 0.011	O(3)-Si(1)-O(4)	$110^\circ 30'$
		O(4)-O(5)	$2.481 \pm 0.014 \text{ \AA}$	O(4)-Si(2)-O(5)	99°
Si(2)-O(4)	$1.673 \pm 0.007 \text{ \AA}$	O(4)-O(6)	2.553 ± 0.014	O(4)-Si(2)-O(6)	$100^\circ 27'$
Si(2)-O(5)	1.588 ± 0.013	O(4)-O(7)	2.673 ± 0.011	O(4)-Si(2)-O(7)	$108^\circ 48'$
Si(2)-O(6)	1.648 ± 0.014	O(5)-O(6)	2.782 ± 0.017	O(5)-Si(2)-O(6)	$118^\circ 32'$
Si(2)-O(7)	1.614 ± 0.009	O(5)-O(7)	2.708 ± 0.016	O(5)-Si(2)-O(7)	$115^\circ 29'$
		O(6)-O(7)	2.703 ± 0.017	O(6)-Si(2)-O(7)	$111^\circ 55'$
				Si(1)-O(4)-Si(2)	$158^\circ 40' \pm 40'$

Table 12. Cell dimensions of pyrosilicates of Eu, Sm, Nd, Ce and La

	<i>a</i>	<i>b</i>	<i>c</i>
$Eu_2Si_2O_7$	$5.374 \pm 0.005 \text{ \AA}$	$12.82 \pm 0.02 \text{ \AA}$	$8.65 \pm 0.01 \text{ \AA}$
$Sm_2Si_2O_7$	5.384 ± 0.005	12.85 ± 0.02	8.69 ± 0.01
$Nd_2Si_2O_7$	5.394 ± 0.005	12.95 ± 0.01	8.72 ± 0.01
$Ce_2Si_2O_7$	5.400 ± 0.005	13.05 ± 0.02	8.73 ± 0.01
$La_2Si_2O_7$	5.410 ± 0.005	13.17 ± 0.02	8.76 ± 0.01

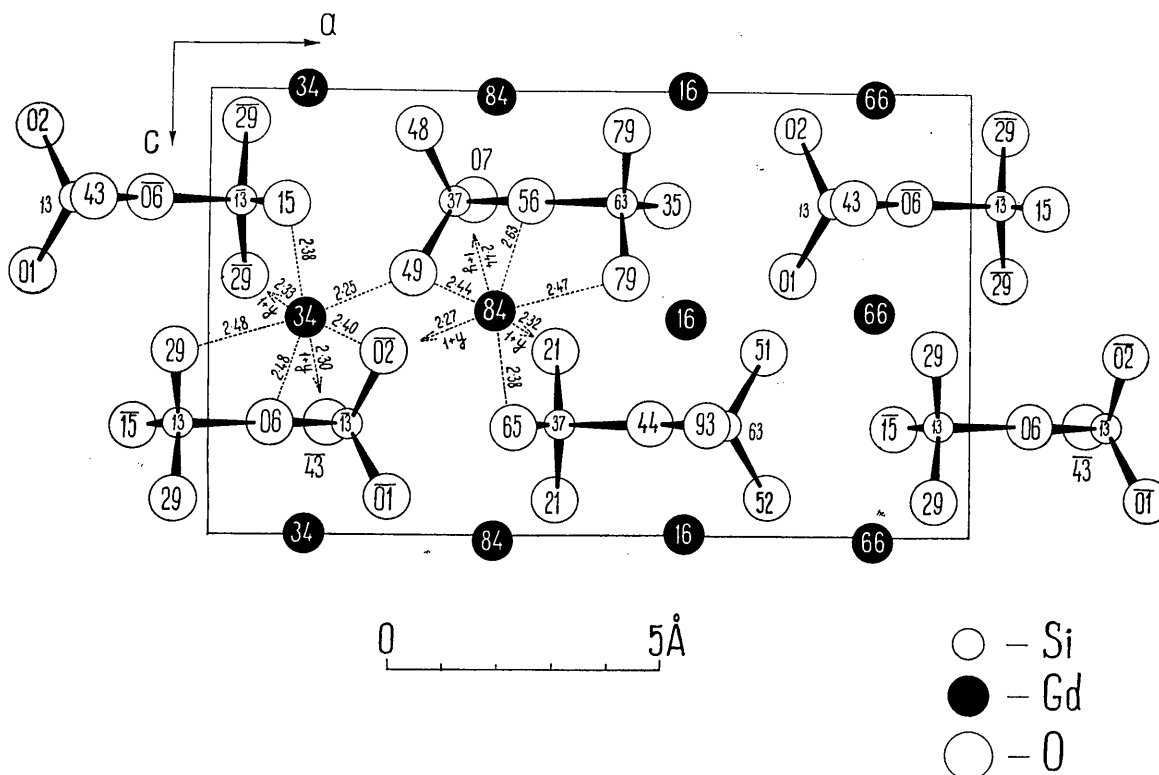


Fig. 3. The structure of $Gd_2Si_2O_7$ projected along the *b* axis.

Intensity data were collected for layers 0-9 around the c axis (1820 reflexions). With the use of the usual Patterson function the Nd atoms were located. The silicon and oxygen atoms were found from two successive three-dimensional Fourier syntheses. A further refinement of three-dimensional data was based on the method of least-squares using a weighting scheme suggested by Cruickshank *et al.* (1961) and the scattering factors for Nd, Si and O (Cromer & Waber, 1965). Correction for dispersion was made for Nd. This refinement gave the final $R=0.077$. The final parameters are listed in Table 13.

The structure of $\text{Nd}_2\text{Si}_2\text{O}_7$ is shown in Fig. 4. The x parameters of the atoms and the coordination of Nd are represented. Each Nd atom is surrounded by eight oxygen atoms. The coordination polyhedra are formed only by terminal oxygen atoms of the pyrosilicate groups. Each of the O(2), O(3), O(5) and O(6) oxygen atoms, as well as being bonded to a silicon atom, are also coordinated to three Nd ions. The O(4) and O(7) oxygen atoms are each coordinated to two Nd ions. The interatomic distances of the cations are given in Table 14.

Table 15 reports the bond lengths and angles in the pyrosilicate group.

In the $\text{Nd}_2\text{Si}_2\text{O}_7$ structure, the pyrosilicate group has bridging bonds differing in length. This asymmetry can probably be explained by different degrees of polarization of the terminal Si-O bonds. Thus, at almost equal average values of these bond lengths (1.631 and 1.630 Å) in different tetrahedra of the pyrosilicate group, one of the tetrahedra has two outer bonds which are short - 1.604 and 1.616 Å - and one bond that is markedly longer - 1.669 Å, where - as all the outer three bonds of another tetrahedron are approximately equal. The occurrence of the two short terminal bonds in one of the tetrahedra can be supposed to be responsible for a decrease in the order of the corresponding bridging bond, compared with the other bond. The mean value of the terminal Si-O bonds is 1.630 Å. As in the $\text{Gd}_2\text{Si}_2\text{O}_7$ structure, the shortest O-O edges of the Si_2O_7 tetrahedra are shared with the Nd polyhedra [O(2)-O(3), 2.614; O(2)-O(4), 2.563; O(5)-O(6), 2.600; O(5)-O(7), 2.538 Å].

Discussion

Some general conclusions are presented here concerning the major factors defining the change in the structure types and the bond orders in the pyrosilicate

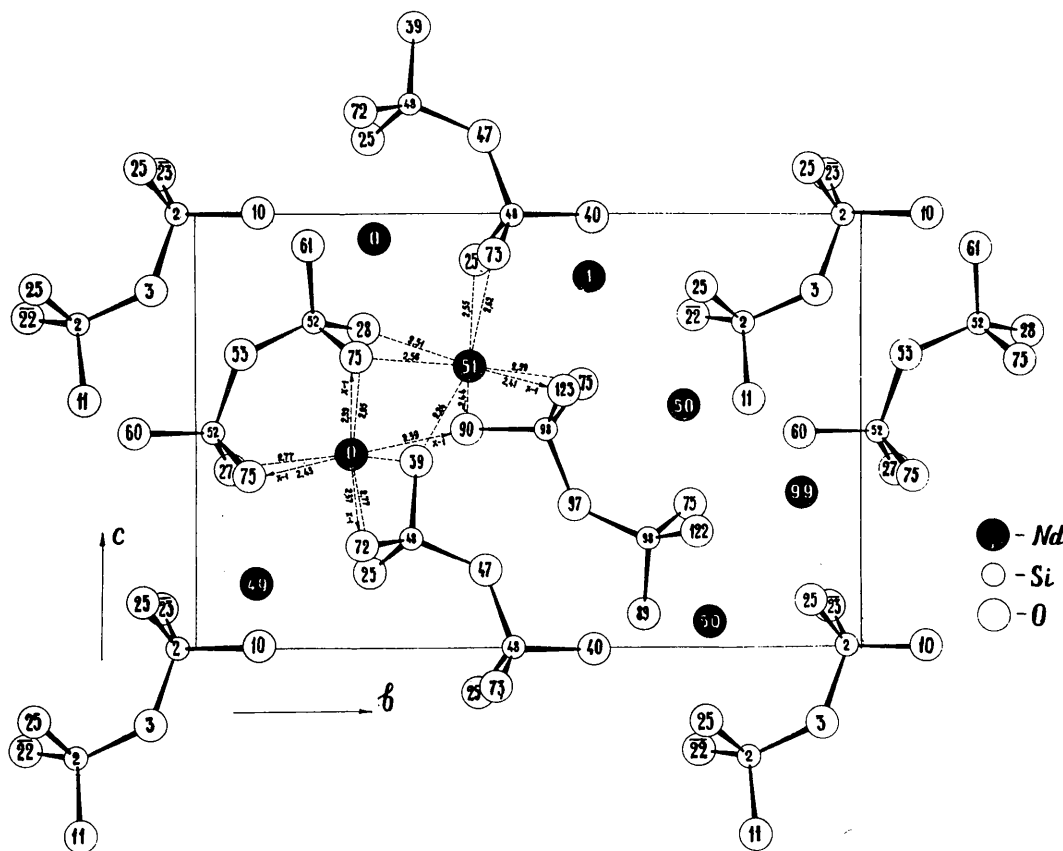


Fig. 4. The structure of $\text{Nd}_2\text{Si}_2\text{O}_7$ projected along the a axis.

groups. The series of the structures determined is, in our opinion, a good illustration of Belov's ideas on the major role of cation size in the formation of a structure type and on the great adaptability of the silicate anions to these sizes. Indeed, in the series of rare earth cations which are similar in their chemical properties, the variation of cation size from Sc (0.68 Å) to La (1.14 Å) leads to a sequence of four structure types having the following cation coordination numbers: 6 for the thortveitite type, 6 for the $\text{Er}_2\text{Si}_2\text{O}_7$ type, 7 for the $\text{Gd}_2\text{Si}_2\text{O}_7$ type and 8 for pyrosilicates of the lanthanides, which have the largest ionic radii. The configuration of the pyrosilicate ions changes to provide the appropriate coordination number for the cation.

In recent years, the simple π -bonding theory, which works well for organic compounds, was used by Cruickshank (1961) and others (Pant & Cruickshank, 1968; McDonald & Cruickshank, 1967) to explain the observed bond lengths in the silicate anions. It is based on the use of the vacant $3d$ orbitals of silicon

for building the π -bonds with oxygen atoms having lone electron pairs. In such an approach the σ -bond system is treated as rigid and unpolarized, with its electron levels lying deeper than those of the π -bond system. A variation of the bond order is due only to a variation in the π -bond potential. The value of the ($p \rightarrow d$) π -interaction in the bridging Si-O bonds of the pyrosilicate group increases with an opening of the Si-O-Si angle, and reaches a limit when this angle equals 180° .

The simple π -bonding theory is apparently insufficient for the compounds under consideration. Thus, in the discussion of the $\text{Sc}_2\text{Si}_2\text{O}_7$ structure (Cruickshank *et al.*, 1962) the bond lengths could be satisfactorily explained only by the assumption that a strong interaction occurs between the terminal oxygen atoms of the pyrosilicate group and the cations.

Attempts are made here to show that in the rare earth pyrosilicate series, to which $\text{Sc}_2\text{Si}_2\text{O}_7$ is also related, the major factor responsible for the Si-O bond orders in the pyrosilicate groups is the polarizing

Table 13. Atomic coordinates with *e.s.d.*'s and isotropic temperature factors for $\text{Nd}_2\text{Si}_2\text{O}_7$

	x/a	$\sigma(x/a)$	y/b	$\sigma(y/b)$	z/c	$\sigma(z/c)$	B
Nd(1)	0.99736	0.00022	0.23136	0.00003	0.44325	0.00007	0.45 Å ²
Nd(2)	0.50719	0.00016	0.40960	0.00003	0.64617	0.00007	0.45
Si(1)	0.4770	0.0006	0.3218	0.0002	0.2494	0.0005	0.52
Si(2)	0.4767	0.0006	0.4748	0.0002	-0.0018	0.0004	0.52
O(1)	0.4710	0.0014	0.4340	0.0005	0.1758	0.0012	0.60
O(2)	0.2500	0.0017	0.2593	0.0006	0.1696	0.0014	0.66
O(3)	0.7232	0.0018	0.2487	0.0007	0.2325	0.0016	0.90
O(4)	0.3947	0.0021	0.3301	0.0008	0.4291	0.0018	1.34
O(5)	0.2534	0.0016	0.4205	0.0006	-0.1070	0.0013	0.54
O(6)	0.7302	0.0019	0.4485	0.0008	-0.0926	0.0014	0.89
O(7)	0.3970	0.0018	0.5941	0.0007	-0.0050	0.0015	0.96

Table 14. Nd-O interatomic distances with *e.s.d.*'s

Nd(1)-O(2)	2.772 ± 0.011 Å	Nd(2)-O(2)	2.557 ± 0.008 Å
Nd(1)-O(2')	2.385 ± 0.011	Nd(2)-O(3)	2.513 ± 0.009
Nd(1)-O(3)	2.370 ± 0.012	Nd(2)-O(4)	2.239 ± 0.014
Nd(1)-O(3')	2.949 ± 0.013	Nd(2)-O(5)	2.554 ± 0.010
Nd(1)-O(4)	2.498 ± 0.011	Nd(2)-O(5')	2.592 ± 0.008
Nd(1)-O(5)	2.427 ± 0.010	Nd(2)-O(6)	2.625 ± 0.012
Nd(1)-O(6)	2.772 ± 0.010	Nd(2)-O(6')	2.413 ± 0.010
Nd(1)-O(7)	2.386 ± 0.009	Nd(2)-O(7)	2.437 ± 0.010

Table 15. Bond lengths with *e.s.d.*'s and valence angles in the pyrosilicate group

Si(1)-O(1)	1.590 ± 0.008 Å	O(1)-O(2)	2.559 ± 0.011 Å	O(1)-Si(1)-O(2)	105° 32'
Si(1)-O(2)	1.624 ± 0.010	O(1)-O(3)	2.803 ± 0.011	O(1)-Si(1)-O(3)	120° 34'
Si(1)-O(3)	1.638 ± 0.011	O(1)-O(4)	2.620 ± 0.015	O(1)-Si(1)-O(4)	108° 47'
Si(1)-O(4)	1.632 ± 0.015	O(2)-O(3)	2.614 ± 0.014	O(2)-Si(1)-O(3)	106° 31'
Si(1)-O(1)	1.636 ± 0.011	O(2)-O(4)	2.563 ± 0.015	O(2)-Si(1)-O(4)	103° 50'
Si(2)-O(5)	1.669 ± 0.010	O(3)-O(4)	2.682 ± 0.017	O(3)-Si(1)-O(4)	110° 10'
Si(2)-O(6)	1.616 ± 0.009	O(1)-O(5)	2.736 ± 0.015	O(1)-Si(2)-O(5)	111° 45'
Si(2)-O(7)	1.604 ± 0.010	O(1)-O(6)	2.733 ± 0.015	O(1)-Si(2)-O(6)	114° 17'
		O(1)-O(7)	2.634 ± 0.013	O(1)-Si(2)-O(7)	108° 47'
		O(5)-O(6)	2.600 ± 0.013	O(5)-Si(2)-O(6)	104° 37'
		O(5)-O(7)	2.538 ± 0.013	O(5)-Si(2)-O(7)	101° 41'
		O(6)-O(7)	2.714 ± 0.014	O(6)-Si(2)-O(7)	114° 55'
				Si(1)-O(1)-Si(2)	132° 36' ± 40'

Table 16. Mean distances for Ln-O, O(terminal)-Si, Si-O(bridge), and the Si-O-Si angles

	Ln-O	O(terminal)-Si	Si-O(bridge)	Si-O-Si
Yb ₂ Si ₂ O ₇	2.237 Å	1.626 Å	1.626 Å	180°
Er ₂ Si ₂ O ₇	2.262	1.617	1.631	180°
Gd ₂ Si ₂ O ₇	2.40	1.614	1.672	158°40'
Nd ₂ Si ₂ O ₇	2.532	1.630	1.613	132°36'

effect of the cations. Table 16 gives the mean value for Ln-O, terminal O-Si and bridge Si-O distances in these compounds.

As seen from Table 16, at the transition from Yb₂Si₂O₇ to Er₂Si₂O₇, where the configurations of pyrosilicate groups and the coordination polyhedra are similar, an increase in cation size results in a lengthening of the cation-oxygen distances. This in turn reduces the degree of polarization of the terminal Si-O bonds. An increase in the order of the outer bonds in the pyrosilicate group leads to a decrease in the order of the inner Si-O bonds without a change in the valency angle, provided the π -bond order remains the same. A transition to another type is associated with an increase in the cation coordination number from 6 to 7. This increase is accomplished through the inclusion of the bridging oxygen atom of the pyrosilicate groups into the coordination polyhedra of two cations. Each of the terminal oxygen atoms is bonded, as before, to two cations. The Si-O-Si angle of the pyrosilicate group was reduced to 158°40' and this could have been regarded as the reason for the sharp decrease in the order of the bridging bonds (see Table 16) on account of the reduced degree of overlap of the oxygen 2p orbitals with the silicon 3d-orbitals. However, such a sharp change in bond length is likely to be caused by the polarization effect of cations as far as the bridge oxygen atom is included in the coordination sphere of gadolinium ions. Indeed, in the Nd₂Si₂O₇ structure the valency angle Si-O-Si was reduced to 132°36' (a further decrease in the π -bonding potential); however the bridge oxygen atom left the cation coordination and the Si-O (bridge) bond lengths decreased (an extremely important observation) and became shorter than those in the pyrosilicate anions with a linear Si-O-Si bridge. It seems likely that the reason for this lies in the fact that an increase in the coordination number of the terminal oxygen atoms leads to a greater degree of polarization of the outer Si-O bonds, their order decreasing here. This in turn causes a corresponding increase in the order of the inner Si-O bonds. By means of the simple π -bonding theory, it is rather difficult to explain the difference in the bridging bond lengths of the pyrosilicate group in the Nd₂Si₂O₇ struc-

ture which can be due (as mentioned above) to a different degree of polarization of the outer bonds.

Taking all the above into consideration, it may be concluded that the bond lengths in the silicate anions of the rare earth pyrosilicates are defined chiefly by the geometry of their arrangement relative to the cations, and this determines the degree of the polarization of the bonds.

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