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Short Communication

X-Ray Crystallographic Study of $Ce_2Si_2O_7$

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The high-temperature form of the rare-earth disilicates $RE_2Si_2O_7$ (RE = La, Ce, Pr, Nd) has a monoclinic structure called type *G*. The structure is described in space group $P2_1/c$ with $Z = 4$. The crystal structure of type *G* has been reported previously from single-crystal X-ray analysis ($Pr_2Si_2O_7$,[1] $Nd_2Si_2O_7$[2]), from X-ray powder diffraction analysis ($La_2Si_2O_7$[3]) and from neutron powder diffraction analysis, ($La_2Si_2O_7$[4] and $Ce_2Si_2O_7$[4]). In the type *G* structure the $Si_2O_7^{6-}$ ion has an Si–O–Si angle of 130–133°, and it should be expected that the Si–O bridge distances would be slightly longer than the Si–O terminal distances. However, the results of the previous structure analysis of the type *G* structure do not give a clear indication of that (Table 1). In the type *G* structure the O bridge atoms are not bonded to the metal atom, and the metal atoms are thus all coordinated with terminal oxygen atoms. This may explain that the Si–O bridge and the Si–O terminal bonds are comparable in length, and that the Si–O bridge distances in some cases appear to be shorter than the Si–O terminal distances. To clarify this matter and to make a structure determination with high precision of a type *G* rare-earth disilicate, a single-crystal X-ray diffraction analysis of the crystal structure of $Ce_2Si_2O_7$ was made.

Table 1. Average distances (in Å) in the $Si_2O_7^{6-}$ ions of the $RE_2Si_2O_7$ structure type *G*.

Compound	Si–O bridge	Si–O terminal	Calculated from Ref.
$La_2Si_2O_7$	1.64	1.63	3
$La_2Si_2O_7$	1.61±2	1.64±2	4
$Ce_2Si_2O_7$	1.61±2	1.63±2	4
$Ce_2Si_2O_7$	1.621±10	1.620±10	This work
$Pr_2Si_2O_7$	1.619±10	1.615±10	1
$Nd_2Si_2O_7$	1.613±10	1.631±10	2

Experimental

The sample of $Ce_2Si_2O_7$ was synthesized as described previously.[4] Precession photographs were taken of a crystal of the sample to ensure that it was a single crystal. The X-ray diffraction data were measured at 25°C on a Huber four-circle diffractometer using Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å). The unit-cell parameters were calculated in a least-squares refinement using diffraction data from 23 high-angle reflections, and these unit-cell parameters and other experimental data are listed in Table 2. Reflections with $I > 3\sigma(I)$ were used in the least-squares refinement of the structure. Starting values for the atomic coordinates were taken from Ref. 4, and the structure was refined using the program LINUS[5] with scattering

Table 2. Experimental data and unit cell parameters for the investigated single crystal of $Ce_2Si_2O_7$

Unit cell parameters	
a/Å	5.4116(7)
b/Å	8.742(2)
c/Å	14.158(3)
β/°	112.26(1)
Cell volume/Å^3	619.87
Space group	$P2_1/c$ (No. 14)
Z	4
Size of crystal/mm	0.125×0.125×0.100
Density (calc.)/g cm^{-3}	4.80
Linear absorption coefficient, μ/cm^{-1}	151
No. of measured reflections	5298
R (intern) of reflections (%)	7.2
No. of independent reflections	4928
No. of reflections with $I > 3\sigma(I)$	2806
Scan method	ω–2θ
Scan range in θ/°	1+0.346 tan θ

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Table 3. Atomic coordinates and equivalent temperature factor parameters for $Ce_2Si_2O_7$.[a]

Atom	x/a	y/b	z/c	$U_{eq} \times 10^{4}$[b]
Ce1	0.51471(12)	0.80856(7)	0.76796(4)	73(2)
Ce2	0.83328(12)	0.60802(6)	0.58957(4)	71(2)
Si1	0.7608(6)	0.2444(4)	0.0266(2)	81(11)
Si2	0.9448(6)	0.4928(3)	0.1796(2)	71(11)
O1	0.8025(17)	0.4197(9)	0.0665(6)	122(31)
O2	1.0475(18)	0.1517(10)	0.0594(7)	156(38)
O3	0.5871(16)	0.1447(9)	0.0753(6)	113(32)
O4	0.5916(21	0.2348(11)	−0.0937(6)	210(39)
O5	0.7641(16)	0.4637(12)	0.2464(6)	157(37)
O6	1.2362(17)	0.4181(11)	0.2428(6)	157(38)
O7	1.0092(19)	0.6713(10)	0.1735(7)	202(39)

[a] Isotropic extinction parameter = 0.19(2).

[b] $U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$.

Table 4. Bond lengths in Å and angles in degrees for $Ce_2Si_2O_7$.

O1–Si1	1.619(8)	Ce1–O7	2.556(10)
O1–Si2	1.622(8)	Ce1–O2	2.706(9)
O2–Si1	1.653(9)	Ce1–O6	2.775(10)
O3–Si1	1.615(8)	Ce1–O5	2.784(10)
O4–Si1	1.602(9)	Ce2–O7	2.276(9)
O5–Si2	1.617(8)	Ce2–O2	2.458(9)
O6–Si2	1.626(9)	Ce2–O3	2.548(8)
O7–Si2	1.608(9)	Ce2–O6	2.550(8)
Ce1–O4	2.400(9)	Ce2–O4	2.573(11)
Ce1–O6	2.434(9)	Ce2–O5	2.589(8)
Ce1–O5	2.488(9)	Ce2–O3	2.589(8)
Ce1–O3	2.514(8)	Ce2–O2	2.656(9)
O1–Si1–O2	112.0(5)	O1–Si2–O6	112.6(5)
O1–Si1–O3	112.9(4)	O1–Si2–O7	111.1(5)
O1–Si1–O4	111.6(5)	O5–Si2–O6	106.9(4)
O2–Si1–O3	104.6(5)	O6–Si2–O7	103.6(5)
O3–Si1–O4	104.2(5)	O7–Si2–O5	112.0(5)
O4–Si1–O2	111.2(5)	Si1–O1–Si2	132.0(5)
O1–Si2–O5	111.4(5)		

contributions from neutral atoms.[6] The weights used in the refinement were $1/\sigma(I)$, yielding the final R-values: $R = 7.0\%$, $R_w = 7.1\%$. The atomic coordinates and thermal parameters are listed in Table 3, and selected interatomic distances and bond angles are listed in Table 4. A stereoscopic drawing of the structure is displayed in Fig. 1.

Discussion

The main purpose of the investigation was to get a structure determination with higher precision than the previous investigation,[4] especially with respect to the geometry of the $Si_2O_7^{6-}$ ion. The precision obtained is significantly better than that from the neutron powder diffraction analysis of the structure of $Ce_2Si_2O_7$.[4] Concerning the geometry of the $Si_2O_7^{6-}$ ion the following average distances were found: Si–O bridge 1.621 ± 10 Å, Si–O terminal 1.620 ± 10 Å. These two average distances are thus not significantly different from each other. This was also observed in the neutron powder diffraction analysis of the structure of $Ce_2Si_2O_7$.[4] The two cerium atoms are each coordinated with eight oxygen atoms. The CeO_8 coordination polyhedra are slightly distorted cubes. The Ce–O bond distances are in the range 2.28–2.78 Å, which is comparable with the bond distances in Sazhinite, $Na_2Ce[Si_6O_{14}(OH)]\cdot nH_2O$, where the Ce–O bond range is 2.29–2.94 Å in the CeO_7 coordination polyhedron.[7]

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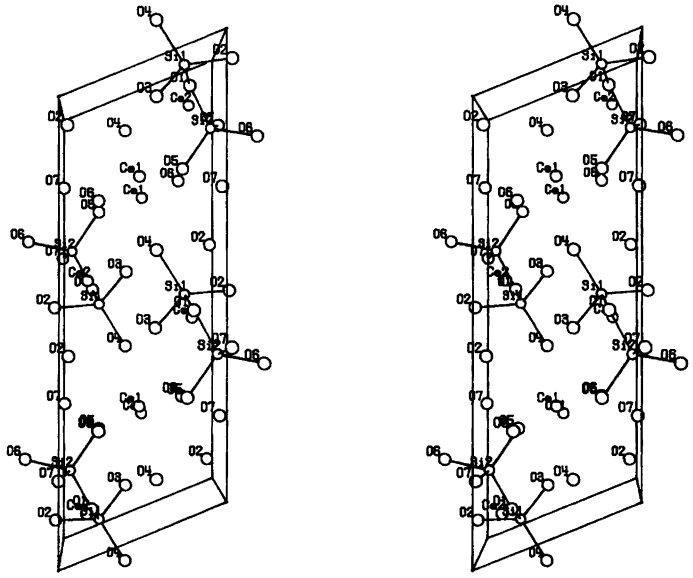

Fig. 1. Projection of the structure of $Ce_2Si_2O_7$, type *G*, along [010]. The *c*-axis is vertical.

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