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## The crystal Structure of SrZrSi<sub>2</sub>O<sub>7</sub>

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**Abstract.** Strontium zirconium disilicate, SrZrSi<sub>2</sub>O<sub>7</sub>,  $M_r = 347.011$ , monoclinic,  $P2_1/c$ ,  $T = 295$  K,  $a = 7.7617(9)$ ,  $b = 8.0713(10)$ ,  $c = 10.0559(11)$  Å,  $\beta = 111.90(1)^\circ$ ,  $V = 584.51(7)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 3.935(1)$  Mg·m<sup>-3</sup>,  $D_{exp} = 3.928(22)$  Mg·m<sup>-3</sup> ( $T = 294.85$  K). Rietveld refinement using neutron powder diffraction data [ $\lambda = 2.5717(3)$  Å,  $F(000) = 252.45$  fm,  $\mu R = 0.11$ , 295 contributing reflections] resulted in  $R_{wp} = 2.72\%$ . The structure can be described by alternately stacking layers containing the ZrO<sub>6</sub> octahedra and layers formed by the Si<sub>2</sub>O<sub>7</sub> groups, parallel to (001). Elongated cages are formed for Sr with distorted SrO<sub>8</sub> dodecahedrons. The Si<sub>2</sub>O<sub>7</sub> groups are in a nearly eclipsed configuration. The title compound is isostructural with the high temperature form of NaFeP<sub>2</sub>O<sub>7</sub>.

**Introduction.** The silicates of strontium are of little or no geothermal interest, and have therefore not been studied very carefully. Knowledge of strontium silicates, however, has become increasingly important as they may play a role in nuclear safety studies. When during very severe nuclear accidents the reactor core has melted through the reactor vessel, the formation of strontium silicates may occur. The abundant presence of zirconium from the fuel cladding and silica in the concrete may lead to the formation of  $\text{SrZrSi}_2\text{O}_7$ .

$\text{SrZrSi}_2\text{O}_7$  is found in the pseudo-binary section  $\text{SrSiO}_3\text{-ZrSiO}_4$ . The existence of  $\text{SrZrSi}_2\text{O}_7$  was first reported by Ghanbari-Ahari and Brett (1988) who studied phase relations in the ternary system  $\text{SrO-SiO}_2\text{-ZrO}_2$ . Their unindexed  $d$ -values also obtained with X-ray powder diffraction agree nicely with ours. In order to understand the chemical activity of this compound better in complex systems such as  $\text{SrO-SiO}_2\text{-ZrO}_2$ , its crystallographic structure has been studied.

**Experimental.**  $\text{SrZrSi}_2\text{O}_7(\text{s})$  was prepared in two steps. In the first step  $\text{SrCO}_3(\text{s})$  (Cerac) was slowly dissolved in  $\text{HNO}_3$  and mixed with alcohol and a calculated amount of TEOS(1) (tetraethyl orthosilicate, Merck). After precipitation with ammonia the sample was dried in an oven (353 K) and decomposed in purified oxygen in a gold boat at 1073 K (Ueno, A., Hayashi, S., Okada, K. & Otsuka, N., 1990). In the second step a calculated stoichiometric amount of  $\text{ZrO}_2(\text{s})$  (Aldrich, <200 ppm Hf) was added to the mixture, followed by heating the sample in a platinum boat in a purified argon atmosphere. After each heating the sample was ground in an alundum mortar and analyzed by X-ray diffraction. This was repeated at gradually higher temperatures up to 1673 K until the sample was phase-pure. In a final heating the sample was heated in a gold boat in purified oxygen at 973 K to compensate for possible oxygen loss during the previous heatings.

The density of  $\text{SrZrSi}_2\text{O}_7$  was measured with double distilled carbon tetrachloride ( $\text{CCl}_4$ , Merck) in a pycnometer with a contents of c.  $25 \text{ cm}^3$ . Per experiment between 2 and 5 gram compound was used to reduce the temperature dependency. Afterwards the  $\text{SrZrSi}_2\text{O}_7$  was checked with X-ray diffraction, but no change in structure could be observed.

The X-ray powder diffraction pattern was obtained with a Philips PW 1130/90 generator

and a Delft Instruments Guinier-de Wolff camera using  $Cu-K\alpha_1$  radiation with  $\lambda = 1.540598 \text{ \AA}$ . A mixture of silicon and tungsten was used as an internal standard. Si from NBS (now designated NIST), standard reference material (SRM) 640a with  $a_0 = 5.430825 (36) \text{ \AA}$  (Hubbard, (1983), and W from Schuchardt, with  $a_0 = 3.16540(9) \text{ \AA}$ , converted to the wave length mentioned above (Parrish, 1960). All diffraction lines could be indexed with the ITO method (Visser, 1969) yielding a figure of merit  $F_{20} = 3\%$  (0.008, 41). The absent reflections in the X-ray diffraction pattern indicate the space group  $P2_1/c$ . The lattice parameters and intensity distribution suggest a strong similarity with the high-temperature structure of  $NaFeP_2O_7$  (Gabelica-Robert, Goreaud, Labbe & Raveau, 1982).

Because no single crystals could be obtained, Rietveld's method was used for refinement of neutron powder-diffraction data, gathered with the Petten High-Flux reactor:  $5 < 2\theta < 152.6$  in steps of  $0.1^\circ$ . Neutrons of  $\lambda = 2.5717(3) \text{ \AA}$  were obtained using the beam reflected from (111) planes of a single crystal of copper and reducing the  $\lambda/n$  contamination to less than 0.1% by means of a pyrolytic graphite filter. Soller slits with a horizontal divergence of  $30'$  were placed between the reactor and the monochromator and in front of the four  $^3He$  counters. The sample holder ( $\phi = 10 \text{ mm}$ ) consisted of a V tube filled up with Cd slices and closed with Cu plugs fitted with O-rings. No precautions were taken to avoid preferred orientation. The neutron powder-diffraction results were analyzed with the program *DBW3.2* version 8804 (Wiles & Young, 1982). The structure of high temperature  $NaFeP_2O_7$  (Gabelica-Robert, Goreaud, Labbe & Raveau, 1982) was used as a trial model. Coherent scattering lengths: Sr 7.02, Zr 7.16, Si 4.149, and O 5.805 fm (Koester, Rauch, Herkens & Schroeder, 1981). 61 parameters were used in the refinement: a scale factor, three half-width parameters defining the Gaussian-like shape of the reflections, six background parameters, the counter zero error, the unit-cell parameters, the atomic positional parameters, isotopic thermal parameters. The largest correlation matrix element for structural parameters is 0.46.

**Discussion.** Atomic parameters are given in Table 1 and selected distances in Table 2. The agreement between the observed and the calculated profiles of the data is shown in Fig 1.

The structure can be described (Gabelica-Robert, Goreaud, Labbe & Raveau, 1982) as a cage structure built up from corner sharing  $ZrO_6$  octahedra and  $Si_2O_7$  groups (Fig. 3). The

$\text{Si}_2\text{O}_7$  group is formed from slightly distorted  $\text{SiO}_4$  groups having one common oxygen. The two tetrahedra are in a nearly eclipsed configuration. The Sr ions are in irregular eight coordination.

The disilicates  $\text{A}_2\text{Si}_2\text{O}_7$  (A = lanthanide, Sc, Y) have received some attention in the structural literature. For small A the thortveitite structure has been found (A = Sc, Tb, Tm) in which  $\text{Si}_2\text{O}_7$  groups exist in staggered conformation and A has six coordination. With increasing radii of A the structure changes (Table 4) and the bridged angle Si-O-Si decreases. Also the coordination of A increases (Smolin & Shepelev, 1970). At low temperature for A = La, Pr, Nd, and Sm the  $\text{Ca}_2\text{P}_2\text{O}_7$  structure has been reported (Felsche & Hirsinger, 1969). Mixed disilicates  $\text{AA}'$  are less well known, only  $\text{CaZrSi}_2\text{O}_7$  with deformed Thortveitite ( $\text{Sc}_2\text{Si}_2\text{O}_7$ ) structure (Roelofsen-Ahland & Peterson, 1989) has been studied. The Si-O-Si angle, in this compound, has been decreased to  $147.4^\circ$ . In the title compound the bridged angle is further decreased to  $133.8^\circ$  (Table 3). Replacing Zr at the octahedral site by the much smaller V, as in  $\text{SrVSi}_2\text{O}_7$  [Takeuchi & Joswig, 1967], causes the structure with  $\text{Si}_2\text{O}_7$  groups to become a chain structure build up of  $\text{Si}_4\text{O}_{12}$  groups.

If the relative charge on the oxygen atoms is calculated with Brown's formalism (Brown & Altermatt, 1985):

$$V_i = \sum_j S_{ij} = \sum_j e \frac{(R_0 - R_{ij})}{B}$$

in which  $V_i$  is the relative charge on the ion (i),  $R_0$  bond valence parameter,  $R_{ij}$  is the bond distance and B a constant; both B and  $R_0$  are empirical constants. For the calculation we used for the bond distances Table 2, for B the value 0.37 and 2.118, 1.624, or 1.928 Å for the bond valence parameter of respectively Sr, Si or Zr. The results given in Table 5 show how the long bond distances between Si and O1 only have a relatively small partial contribution to the overall charge on O1.

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## Figure Captions

- Figure 1.** Observed (dots) and calculated (full line) neutron diffraction profile of  $\text{SrZrSi}_2\text{O}_7$  at 295 K. position of nuclear lines and  $I(\text{obs.}) - I(\text{calc.})$  is indicated.
- Figure 2.** A projection along  $[001]$  of  $\text{SrZrSi}_2\text{O}_7$ . The fractional Z coordinates are indicated in parenthesis.
- Figure 3.** An artist impression of the  $\text{SrZrSi}_2\text{O}_7$  structure: in the left part the irregular  $\text{SrO}_8$  dodecahedrons are left out, now showing the cages and the characteristic linkage between the  $\text{Si}_2\text{O}_7$  groups and the  $\text{ZrO}_6$  octahedra.

**Table 1.** Fractional atomic coordinates and thermal parameters ( $\text{\AA}^2$ ) of  $\text{SrZrSi}_7\text{O}_7$  at 295 K.

atom	x	y	z	B
Sr	0.2825(4)	0.4817(4)	0.2945(3)	0.72(10)
Zr	0.2597(5)	0.0110(4)	0.2640(4)	0.48(7)
Si(1)	0.0650(8)	0.2484(7)	0.4577(5)	0.22(15)
Si(2)	0.6737(7)	0.2136(7)	0.4605(5)	0.65(17)
O(1)	0.8675(5)	0.1539(5)	0.4390(4)	0.54(12)
O(2)	0.1918(5)	0.2689(5)	0.6250(4)	0.88(10)
O(3)	0.0115(5)	0.4214(4)	0.3695(4)	0.79(12)
O(4)	0.1698(5)	0.1344(5)	0.3809(4)	0.57(14)
O(5)	0.5257(6)	0.0195(5)	0.3492(4)	0.72(11)
O(6)	0.6943(5)	0.2050(5)	0.6239(4)	0.06(12)
O(7)	0.6331(6)	0.4044(4)	0.4064(4)	0.08(11)

$R_p = 2.05\%$ ;  $R_{wp} = 2.72\%$ ;  $DW-d = 1.52$ ;  $\chi^2_{red} = 2.03$ .

**Table 2.** *Atomic distances [Å] and angles [°] in SrZrSi<sub>2</sub>O<sub>7</sub> at 295 K.*

<b>(a) Si1 tetrahedron</b>			
Si-O1 <sup>i</sup>	1.660(7)	O1 <sup>i</sup> -Si-O2	110.2(4)
Si-O2	1.610(6)	O1 <sup>i</sup> -Si-O3	107.3(4)
Si-O3	1.625(6)	O1 <sup>i</sup> -Si-O4	107.7(4)
Si-O4	1.605(7)	O2-Si-O3	114.5(4)
		O2-Si-O4	109.9(4)
		O3-Si-O4	107.7(4)
		Si1-O1 <sup>i</sup> -Si2 <sup>i</sup>	133.8(4)
<b>(b) Si2 tetrahedron</b>			
Si-O1	1.669(7)	O1-Si-O5	100.2(4)
Si-O5	1.609(6)	O1-Si-O6	111.9(3)
Si-O6	1.602(7)	O1-Si-O7	107.6(4)
Si-O7	1.627(6)	O5-Si-O6	117.5(4)
		O5-Si-O7	110.5(3)
		O6-Si-O7	108.6(4)
<b>(c) Zr octahedrons</b>			
Zr-O2 <sup>ii</sup>	2.108(5)	O2 <sup>ii</sup> -Zr-O3 <sup>iii</sup>	89.3(2)
Zr-O3 <sup>iii</sup>	2.118(5)	O2 <sup>ii</sup> -Zr-O4	84.0(2)
Zr-O4	2.007(6)	O2 <sup>ii</sup> -Zr-O5	90.7(2)
Zr-O5	2.042(5)	O2 <sup>ii</sup> -Zr-O6 <sup>iii</sup>	174.0(3)
Zr-O6 <sup>iii</sup>	2.131(5)	O2 <sup>ii</sup> -Zr-O7 <sup>iii</sup>	90.4(2)
Zr-O7 <sup>iii</sup>	2.176(7)	O3 <sup>iii</sup> -Zr-O4	90.9(2)
		O3 <sup>iii</sup> -Zr-O5	176.9(3)
		O3 <sup>iii</sup> -Zr-O6 <sup>iii</sup>	87.8(2)
		O3 <sup>iii</sup> -Zr-O7 <sup>iii</sup>	92.4(2)
		O4-Zr-O5	92.2(2)
		O4-Zr-O6 <sup>iii</sup>	90.8(2)
		O4-Zr-O7 <sup>iii</sup>	173.5(3)
		O5-Zr-O6 <sup>iii</sup>	92.5(2)
		O5-Zr-O7 <sup>iii</sup>	84.5(2)
		O6 <sup>iii</sup> -Zr-O7 <sup>iii</sup>	95.0(2)
<b>(d) Sr dodecahedron</b>			
Sr-O1 <sup>iii</sup>	2.602(5)		
Sr-O2 <sup>ii</sup>	2.571(5)		
Sr-O3	2.533(6)		
Sr-O4	3.157(5)		
Sr-O5 <sup>iii</sup>	2.588(6)		
Sr-O6 <sup>iv</sup>	2.647(5)		
Sr-O7	2.605(5)		
Sr-O7 <sup>v</sup>	2.976(5)		

Symmetry code: (i): 1-x,y,z; (ii): x,½-y,½-z; (iii): 1-x,½+y,½-z; (iv): 1-x,½+y,1-z; (v): 1-x,1-y,1-z.

**Table 3.** *Comparison of interatomic distances and angles in  $A_2Si_2O_7$  and  $AA'Si_2O_7$ .*

substance	coordination of A	terminal Si-O distance [Å]	bridged Si-O distance [Å]	Si-O-Si angle [°]	ref.
$Yb_2Si_2O_7$	6	1.62(2)	1.63(1)	180	a
$Er_2Si_2O_7$	6	1.62(1)	1.63(1)	180	a
$Gd_2Si_2O_7$	7	1.61(1)	1.67(2)	158.7(7)	a
$Nd_2Si_2O_7$	8	1.63(1)	1.61(2)	132.6(7)	a
$CaZrSi_2O_7$	6.8	1.622(7)	1.643(3)	147.4(5)	b
$SrZrSi_2O_7$	6.8	1.613(6)	1.665(7)	133.8(4)	c

a: Smolin & Shepelev. (1970); b: Roelofsen-Ahland & Robertson (1989); c: this study

**Table 4.** *Relative charge on the oxygen atom. according to Browns formalism.*

bonding	$S_{ij}$	bonding	$S_{ij}$
O1-Si1	0.91	O5-Si2	1.04
O1-Si2	0.89	O5-Zr	0.75
O1-Sr	0.27	O5-Sr	0.28
V(O1):	2.07	V(O5):	2.07
O2-Si1	1.04	O6-Si2	1.06
O2-Zr	0.63	O6-Zr	0.59
O2-Sr	0.29	O6-Sr	0.24
V(O2):	1.96	V(O6):	1.89
O3-Si1	1.00	O7-Si2	0.99
O3-Zr	0.61	O7-Zr	0.53
O3-Sr	0.33	O7-Sr	0.27
V(O3):	1.94	O7-Sr	0.10
		V(O7):	1.88
O4-Si1	1.05		
O4-Zr	0.83		
O4-Sr	0.06		
V(O4):	1.94		

Figure 1

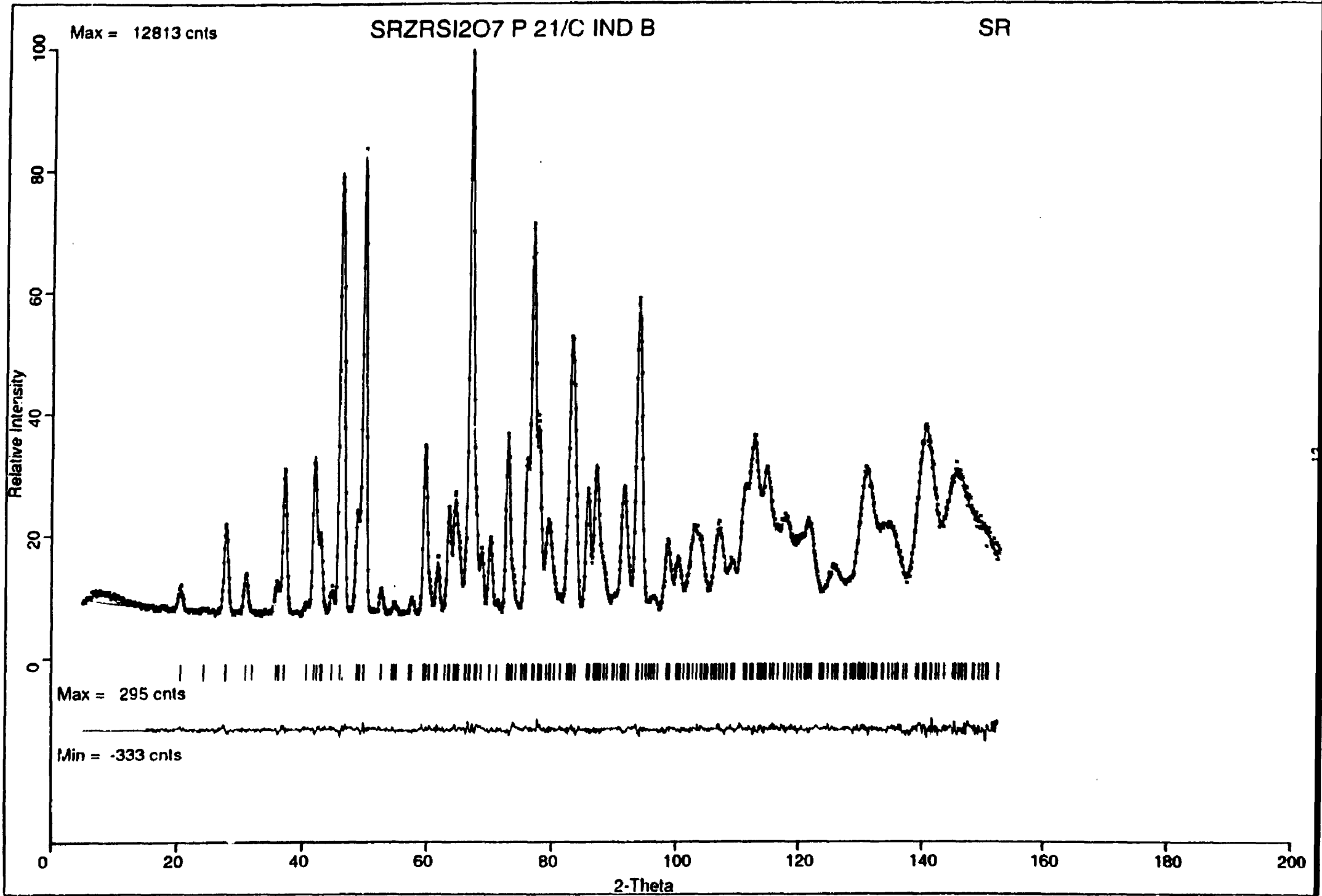


Figure 2

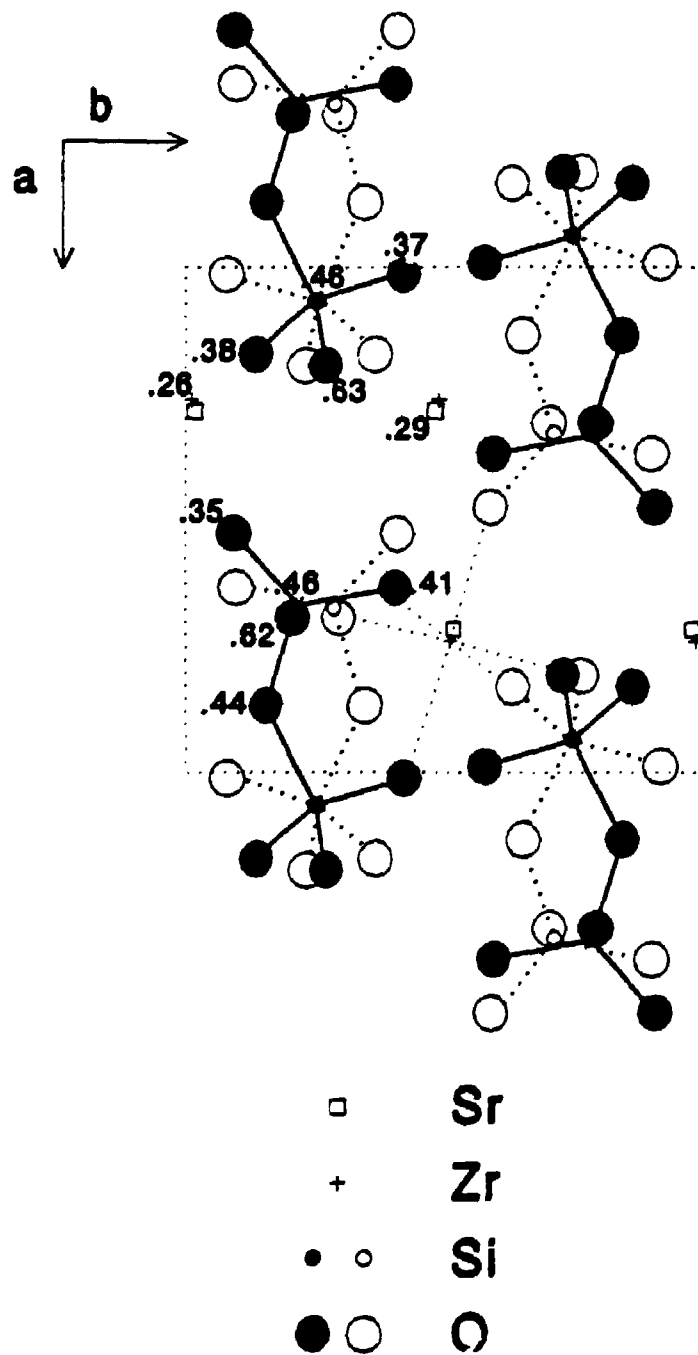


Figure 3

