The crystal structure of rengeite, $Sr_4ZrTi_4(Si_2O_7)_2O_8$

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The crystal structure of rengeite was analyzed with a single crystal of the type specimen; $(Sr_{3.62}Ca_{0.08}Ce_{0.03}Nd_{0.02}Ba_{0.01}Pr_{0.01})_{\Sigma3.76}(Ti_{4.09}Zr_{0.84}Al_{0.04}Fe_{0.02}Nb_{0.02})_{\Sigma5.01}$ $Si_{4.11}O_{22}$, $a = 13.9830(10)$, $b = 5.6722(9)$, $c = 11.9960(10)$ Å, $\beta = 114.215(7)°$, $V = 867.74(17)$ Å³, $Z = 2$. A refinement with space group $P2_1/a$ showed strong correlations between the parameters of oxygen atoms related by pseudo-mirror planes, and gave non-positive mean square displacement parameters for the oxygen atoms. A refinement with space group $P2_1/a$ and isotropic displacement parameters for oxygen atoms was converged to $R1$ [$F_o > 4\sigma(F_o)$] $= 0.0523$. On the other hand, a refinement with space group $C2/m$ and anisotropic displacement parameters, in which several very weak observed reflections were ignored, was successfully converged to $R1 = 0.0485$. No significant differences in atomic parameter could be observed between the refinements with $C2/m$ and $P2_1/a$, except for the x of O(1) site. Although the true space group of rengeite is $P2_1/a$, the space group can be regarded as pseudo-$C2/m$. Rengeite is isostructural with perrierite-(Ce). Zirconium in rengeite occupies preferentially one of three octahedral sites, and does not share the site with Ti. Therefore, the formula of rengeite is not $Sr_4(Ti,Zr)_5(Si_2O_7)_2O_8$, but $Sr_4ZrTi_4(Si_2O_7)_2O_8$. A re-indexing of the XRD data of strontio-chevkinite with reference to those of rengeite suggested that strontio-chevkinite might be an Fe-rich variety of rengeite.

Introduction

Rengeite, $Sr_4ZrTi_4(Si_2O_7)_2O_8$, is a new member of the perrierite group minerals (Miyajima et al., 2001). It occurs as anhedral crystals in the blue and lavender jades from Itoigawa, Niigata Prefecture, Japan. This mineral can be described as a Sr- and Zr-analogue of perrierite -(Ce), $Ce_4FeTi_4(Si_2O_7)_2O_8$, which was described as a new mineral by Bonatti (1950). The chemical composition of rengeite suggests that Zr atoms occupy the largest octahedral site among the three independent octahedral sites in the perrierite structure, as Fe atoms in perrierite-(Ce) do. However, there is a possibility that Zr atoms are distributed into the three octahedral sites with Ti atoms. In this case, the chemical formula of rengeite should be expressed as $Sr_4(Ti,Zr)_5(Si_2O_7)_2O_8$. A crystal structure analysis with refinements of occupancy parameters would clarify this problem. Since, intensity data of X-ray diffraction could be obtained fortunately with the type material of rengeite, we attempted the structure

analysis.

Experimental

The intensity data were collected with a RIGAKU AFC7R diffractometer with graphite monochromatized Mo$K\alpha$ radiation (56 kV, 270 mA). The sample is a single crystal fragment picked up from a thin section of the type specimen (NSM-M27921), which was used in the descriptive study (Miyajima et al., 2001). No heating treatment was carried out, because rengeite does not occur in the metamict state. The crystal with approximate dimensions of $0.20 \times 0.20 \times 0.03$ mm was mounted on a 10 μm ϕ glass fiber. The data were collected with $2\theta-\omega$ scan and the scanning rate of 2°/min (in ω) for 2θ range up to 75°. A total of 2720 reflections were collected, and merging of equivalent reflections gave 2455 unique reflections ($R_{int} = 0.0233$), of which 1937 were classified as observed [$I > 2\sigma(I)$]. The cell parameters refined from 25 reflections with 2θ range between 30 and 35° are; $a = 13.9830(10)$, $b = 5.6722(9)$, $c = 11.9960(10)$ Å, $\beta = 114.215(7)°$, $V = 867.74(17)$ Å³, for which $Z = 2$.

Initial parameters for $C2/m$ and $P2_1/a$ models

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were adopted from the results of crystal structure analyses of perrierite-(Ce) (Gottardi, 1960) and a related synthetic material (Calvo and Faggiani, 1974), respectively. The computer program package for crystal structure analysis 'teXsan' (1993) recommended the C-lattice, and the refinement with the $P2_1/a$ model was not converged. The refinement with the $C2/m$ model was carried out with occupancy parameters fixed for the largest cation sites based on the chemical analysis as follows; $0.960Sr + 0.0176Ce + 0.0226Ca$. The refinement with the scattering curve of Ti for all the octahedral sites gave an unusually smaller isotropic displacement parameter for one of the three octahedral sites in comparison with the other two. The introduction of the Zr-scattering curve to this site improved the anomalous displacement parameter to be compatible with those of the other two octahedral sites. Therefore, this octahedral site was assumed to be occupied by Zr atoms in the subsequent calculations.

The diffraction data were converted into the F^2 data by a computer program written by Sugiyama (personal communication) for further refinements. The ψ-scan technique was applied to the empirical absorption correction (North et al., 1968). SHELXL-97 (Sheldrick, 1997) was employed as the refinement program. Scattering factors for neutral atoms and anomalous dispersion factors were taken from the International Tables for X-ray Crystallography, Volume C (1992).

The refinement with the $C2/m$ model was started with the result of the preliminary analysis. A full-matrix least-squares refinement was performed by refining a scale factor, positional parameters, and isotropic displacement parameters. The site occupancy factors (*sof*) for the Sr and Ti sites were constrained as follows; Sr+Ce=1, and Ti+(Al or Fe)=1. The refinement of *sof* for the Ti(2) site with Ti and Al scattering factors led to an anomalous result, 1.03Ti and –0.03Al, indicating that some other heavier atoms occupy this site in addition to Ti atoms. Consequently, Fe was introduced into this site, instead of Al, according to the chemical analysis. The refinement was converged to $R1 [F_o > 4\sigma(F_o)] = 0.0564$. The final parameters for the refinement with anisotropic displacement parameters for all the atoms in the $C2/m$ model are; $R1 [F_o > 4\sigma(F_o)] = 0.0485$, $R1$(all reflections)=0.0724, $wR2$ (all reflections)=0.1593, Goodness of Fit=1.160, Final $\Delta\rho_{min} = -3.714$, Final $\Delta\rho_{max} = 2.626$ e/Å^3.

The atomic coordinate parameters in the $C2/m$ model were transformed into those in the $P2_1/a$ model, by referring to the parameters given by Calvo and Faggiani (1974). The *sof* for the Sr and Ti sites were fixed in the initial refinement with the $P2_1/a$ model according to the final result of the refinement with the $C2/m$ model, because of an increase in the number of parameter refined with the P-cell, 160 for $P2_1/a$ and

Table 1. Final atomic coordinates, equivalent isotropic displacement parameters, and occupancy parameters for rengeite

the $C2/m$ model					the $P2_1/a$ model			
	x	y	z	U_{eq}		x	y	z	U_{eq}
Sr(1)	0.76861(4)	0.0000	0.73673(5)	0.00919(17)	Sr(1)	0.76860(4)	0.0003(5)	0.73673(5)	0.00926(15)
Sr(2)	0.54661(4)	0.5000	0.74203(5)	0.00967(18)	Sr(2)	0.54661(4)	0.5002(5)	0.74201(5)	0.00972(16)
Zr	0.0000	0.5000	0.5000	0.00604(19)	Zr	0.0000	0.5000	0.5000	0.00608(17)
Ti(1)	0.5000	0.7420(2)	0.0000	0.0080(3)	Ti(1)	0.5000(3)	0.74198(19)	0.9998(5)	0.0082(3)
Ti(2)	0.27341(8)	0.0000	0.00144(10)	0.0079(2)	Ti(2)	0.27342(7)	0.0000(9)	0.00145(9)	0.0079(2)
Si(1)	0.40778(13)	0.0000	0.73618(16)	0.0071(3)	Si(1)	0.40775(12)	0.9985(12)	0.73610(15)	0.0075(3)
Si(2)	0.83743(13)	0.0000	0.45121(16)	0.0069(3)	Si(2)	0.83743(12)	0.0007(13)	0.45119(15)	0.0069(3)
O(1)	<u>0.0655(3)</u>	0.2635(6)	0.1793(3)	0.0089(5)	O(1)	0.0699(6)	0.7383(17)	0.1783(8)	0.0057(17)*
					O(1')	0.0605(7)	0.2655(19)	0.1803(9)	0.0087(19)*
O(2)	0.2095(3)	0.2499(6)	0.8827(3)	0.0085(5)	O(2)	0.2086(10)	0.754(3)	0.8828(14)	0.012(3)*
					O(2')	0.2100(8)	0.253(2)	0.8826(11)	0.005(2)*
O(3)	0.3886(3)	0.7344(6)	0.4143(3)	0.0109(6)	O(3)	0.3886(8)	0.736(2)	0.4137(11)	0.006(2)*
					O(3')	0.3885(11)	0.267(3)	0.4150(16)	0.017(3)*
O(4)	0.0923(4)	0.0000	0.9974(5)	0.0093(8)	O(4)	0.0924(3)	0.001(4)	0.9975(4)	0.0094(7)*
O(5)	0.4059(4)	0.0000	0.0024(4)	0.0078(7)	O(5)	0.4059(3)	0.001(4)	0.0024(4)	0.0079(6)*
O(6)	0.4770(4)	0.0000	0.6576(5)	0.0122(8)	O(6)	0.4771(3)	0.992(3)	0.6575(4)	0.0113(8)*
O(7)	0.2835(4)	0.0000	0.6534(5)	0.0135(9)	O(7)	0.2835(4)	0.005(3)	0.6534(4)	0.0124(8)*
O(8)	0.1474(4)	0.0000	0.4119(4)	0.0108(8)	O(8)	0.1474(3)	0.000(4)	0.4117(4)	0.0109(7)*

Occupancy		Occupancy	
Sr(1)	0.946(9)Sr + 0.054Ce	Sr(1)	0.945(8)Sr + 0.055Ce
Sr(2)	0.977(9)Sr + 0.023Ce	Sr(2)	0.976(8)Sr + 0.024Ce
Ti(1)	0.95(2)Ti + 0.05Al	Ti(1)	0.950(18)Ti + 0.050Al
Ti(2)	0.89(3)Ti + 0.11Fe	Ti(2)	0.90(3)Ti + 0.10Fe

*, isotropic displacement factors.

101 for $C2/m$. Although the refinement with anisotropic displacement parameters for the Sr, Zr, Ti and Si atoms was converged ($R1$ [$F_o > 4\sigma(F_o)$] = 0.0523), the refinement with anisotropic displacement parameters for all the atoms resulted in "non positive definite" for the equivalent isotropic displacement parameters of almost all the oxygen atoms. Therefore, the final refinement with the $P2_1/a$ model was carried out by applying anisotropic displacement factors only to the cations. The *sof* for the Sr and Ti sites were refined with the other parameters under the constraints of Sr+Ce=1, Ti+Al=1, and Ti+Fe=1 for the Sr, Ti(1) and Ti(2) sites, respectively. The final parameters for the $P2_1/a$ model are; $R1$ [$F_o > 4\sigma(F_o)$] = 0.0523, $R1$ (all reflections)=0.1466, w$R2$ (all reflections)=0.1917, Goodness of Fit=1.020, Final $\Delta\rho_{min}$ = −3.724, Final $\Delta\rho_{max}$=2.671 e/Å³.

The final positional parameters and equivalent isotropic displacement parameters are given in Table 1. Table 2 shows anisotropic displacement parameters. The selected interatomic distances and bond angles are summarized in Table 3.

Description of the structure

The positions of atoms in the $P2_1/a$ model are consistent with those in the $C2/m$ model (Table 1). In the $P2_1/a$ model, the O(1), O(2) and O(3) sites in the $C2/m$ model are divided into two sites related by imaginary pseudo-mirror planes at $y=0$ and 0.5. The atomic sites on the mirror planes at $y=0$ and 0.5 in the $C2/m$ model, *i.e.*, the other O sites and all cation sites except for the Ti(1), lose their mirror symmetry in the $P2_1/a$ model. However, the displacements of the sites from the mirror planes are within standard deviations. A significant difference can be observed only in the x

coordinate of O(1) site between the two models.

Rengeite is isostructural with perrierite–(Ce). The crystal structure consists of walls of TiO_6 octahedra, chains of ZrO_6 octahedra, Si_2O_7 disilicate groups, and Sr– polyhedra (Fig. 1). The Ti(1)O_6 and Ti(2)O_6 octahedra form chains by edge–sharing connections parallel to the b axis, respectively. The Ti(1)O_6 and Ti(2)O_6 octahedra share their corners mutually in the direction of the a axis to form the TiO_6 wall parallel to the (001). The chains of ZrO_6 octahedra running parallel to the b axis are located in the middle of two TiO_6 walls. The Si_2O_7 disilicate groups connect the TiO_6 wall and the ZrO_6 chains. The Sr atoms are in the cavities of the framework formed with the walls and chains.

The mean Ti(1)–O distance, 1.945Å in the $C2/m$ model, is shorter than the mean Ti(2)–O distance, 2.020Å (Table 3). This result confirms the occupancies for the Ti(1) and Ti(2) sites; the smaller Al^{3+} ions replace a part of Ti^{4+} ions in the Ti(1) site, whereas Fe (probably Fe^{3+}) ions partially substitute Ti^{4+} ions in the Ti(2) site. The Ti(2)O_6 octahedron is more distorted in comparison with the Ti(1)O_6 octahedron (the longer Ti(2)–O(4) and the shorter Ti(2)–O(5) distances, Table 3). The distortion of the Ti(2)O_6 octahedron in rengeite is consistent with the characteristic difference of the perrierite structure from the chevkinite structure pointed out by Calvo and Faggiani (1974).

The Si(1)–O(7)–Si(2) angle, through the bridging oxygen atom of the Si_2O_7 disilicate group, is approximately 170°, and is less significantly bended than those in $La_4Mg_2Ti_3(Si_2O_7)_2O_8$ [perrierite type] (165.6°), $Nd_4Mg_2Ti_3(Si_2O_7)_2O_8$ [chevkinite type] (157.4°), and $Nd_4Co_2Ti_3(Si_2O_7)_2O_8$ [chevkinite type] (157.3°) (Calvo and Faggiani, 1974). The displacement parameters for the bridging O(7) is the largest among the O sites in rengeite structure, as pointed out by Calvo and Faggiani

Table 2. Final anisotropic displacement parameters ($\times 10^4$) of rengeite

the $C2/m$ model

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Sr(1)	78(2)	101(3)	99(3)	0	383(18)	0
Sr(2)	77(2)	120(3)	95(3)	0	366(18)	0
Zr	58(3)	55(3)	73(3)	0	30(2)	0
Ti(1)	95(5)	78(5)	60(5)	0	24(3)	0
Ti(2)	84(4)	68(4)	87(4)	0	36(3)	0
Si(1)	61(6)	72(7)	86(7)	0	36(5)	0
Si(2)	56(6)	53(6)	91(7)	0	23(5)	0
O(1)	119(12)	68(12)	63(11)	4(9)	19(10)	-11(11)
O(2)	104(11)	80(12)	61(11)	-17(10)	25(9)	-15(11)
O(3)	112(12)	89(13)	120(13)	0(11)	42(10)	-45(11)
O(4)	104(17)	60(17)	119(19)	0	50(15)	0
O(5)	80(16)	68(17)	102(18)	0	53(14)	0
O(6)	106(18)	170(20)	119(19)	0	76(16)	0
O(7)	57(16)	150(20)	150(20)	0	-4(15)	0
O(8)	122(18)	118(19)	80(17)	0	37(15)	0

the $P2_1/a$ model

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Sr(1)	79(2)	102(2)	99(2)	15(9)	392(16)	26(8)
Sr(2)	77(2)	120(3)	95(2)	-2(9)	363(16)	25(8)
Zr	58(3)	55(3)	73(3)	15(12)	31(2)	10(11)
Ti(1)	97(4)	82(5)	60(4)	-16(16)	25(3)	-52(15)
Ti(2)	83(4)	69(4)	86(4)	-19(15)	35(3)	3(14)
Si(1)	62(6)	78(7)	93(7)	80(20)	40(5)	20(20)
Si(2)	57(5)	55(6)	90(6)	-30(20)	22(5)	10(20)

Table 3. Interatomic distances (Å) and bond angles (°) of rengeite

the $C2/m$ model							the $P2_1/a$ model					
Sr(1) — O(8)	2.505(5)		Sr(2) — O(8)	2.580(5)			Sr(1) — O(8)	2.504(5)		Sr(2) — O(1')	2.554(9)	
— O(1)	2.591(3)	x2	— O(1)	2.607(3)	x2		— O(1)	2.539(9)		— O(8)	2.580(4)	
— O(2)	2.637(3)	x2	— O(2)	2.625(3)	x2		— O(2')	2.621(12)		— O(2)	2.605(15)	
— O(3)	2.667(4)	x2	— O(3)	2.738(4)	x2		— O(1')	2.650(9)		— O(2')	2.639(12)	
— O(4)	2.977(5)		— O(4)	2.861(5)			— O(2)	2.657(14)		— O(1)	2.656(9)	
— O(7)	3.043(2)	x2	— O(6)	3.0343(19)	x2		— O(3)	2.661(12)		— O(3)	2.736(11)	
<Sr(1)—O>$_8$	2.659		<Sr(2)—O>$_8$	2.673			— O(3')	2.675(17)		— O(3')	2.741(16)	
<Sr(1)—O>$_{10}$	2.736		<Sr(2)—O>$_{10}$	2.745			— O(4)	2.977(4)		— O(4)	2.862(4)	
							— O(7)	3.013(18)		— O(6)	2.992(16)	
							— O(7)	3.072(18)		— O(6)	3.077(16)	
							<Sr(1)—O>$_8$	2.661		<Sr(2)—O>$_8$	2.672	
							<Sr(1)—O>$_{10}$	2.737		<Sr(2)—O>$_{10}$	2.744	
Zr — O(6)	2.044(5)	x2					Zr — O(6)	2.043(5)	x2			
— O(3)	2.107(3)	x4					— O(3)	2.103(12)	x2			
<Zr —O>	2.086						— O(3')	2.113(17)	x2			
							<Zr —O>	2.086				
Ti(1) — O(4)	1.893(3)	x2	Ti(2) — O(5)	1.848(5)			Ti(1) — O(4)	1.891(16)		Ti(2) — O(5)	1.848(4)	
— O(1)	1.965(3)	x2	— O(2)	1.931(3)	x2		— O(4)	1.896(16)		— O(2')	1.920(13)	
— O(5)	1.976(3)	x2	— O(2)	1.947(3)	x2		— O(1)	1.959(10)		— O(2)	1.933(16)	
<Ti(1)—O>	1.945		— O(4)	2.513(5)			— O(5)	1.973(16)		— O(2)	1.945(16)	
			<Ti(2)—O>	2.020			— O(1')	1.975(11)		— O(2')	1.960(13)	
							— O(5)	1.979(16)		— O(4)	2.512(4)	
							<Ti(1)—O>	1.946		<Ti(2)—O>	2.020	
Si(1) — O(6)	1.604(5)		Si(2) — O(8)	1.568(5)			Si(1) — O(6)	1.606(5)		Si(1) — O(8)	1.569(5)	
— O(7)	1.609(5)		— O(7)	1.641(5)			— O(1')	1.608(11)		— O(3')	1.639(17)	
— O(1)	1.630(3)	x2	— O(3)	1.654(4)	x2		— O(7)	1.609(5)		— O(7)	1.642(5)	
<Si(1)—O>	1.618		<Si(2)—O>	1.629			— O(1)	1.655(11)		— O(3)	1.666(13)	
							<Si(1)—O>	1.620		<Si(2)—O>	1.629	
Si(1)—O(7)—Si(2) 170.0(4)							Si(1)—O(7)—Si(2) 169.7(5)					

The mean distance is given in the last of each data set of polyhedron.

(1974) for those in the synthetic materials with perrierite or chevkinite structure.

The coordination polyhedra of the larger Sr^{2+} ions can be described as SrO_{10}-polyhedra for the Sr(1) and Sr(2) sites. Although the maximum Sr–O distances exceed 3 Å, the mean Sr–O distances, 2.763 Å, are comparative to the sum of effective ionic radii (Shannon and Prewitt, 1969) of 10-coordinated Sr^{2+} and O^{2-} ions, 1.32 and 1.40 Å, respectively.

Discussion

The crystal structures of chevkinite–(Ce) and perrierite –(Ce) were determined with space group $C2/m$ by Pen and Pan (1964) and Gottardi (1960), respectively.

Calvo and Faggiani (1974) successfully refined the two structures using synthetic samples with space group $P2_1/a$ as suggested by Ito and Arem (1971). The crystal structures of chevkinite–(Ce) and perrierite–(Ce) are essentially the same, and their crystallo–chemical formula can be expressed as $A_4BC_2Ti_2(Si_2O_7)_2O_8$, where $A = Ce^{3+}, La^{3+}, Th^{4+}, Ca^{2+}, Na^+$ and the other rare earths, $B = Fe^{2+}, Mg^{2+}, Ca^{2+}$ and the other transition metals, $C = Ti^{4+}, Fe^{3+}, Fe^{2+}, Mg^{2+}$. The crystal structure of chevkinite–(Ce) can be essentially derived from that of perrierite–(Ce) with the transformation of a unit cell by a matrix of $(-1, 0, 0; 0, 1, 0; 0.5, 0, 1)$ and shifting the origin to $(0, 0, 0.5)$. Calvo and Faggiani (1974) pointed out that the distribution of Ti and Mg(Co) among the available octahedral sites differs between the
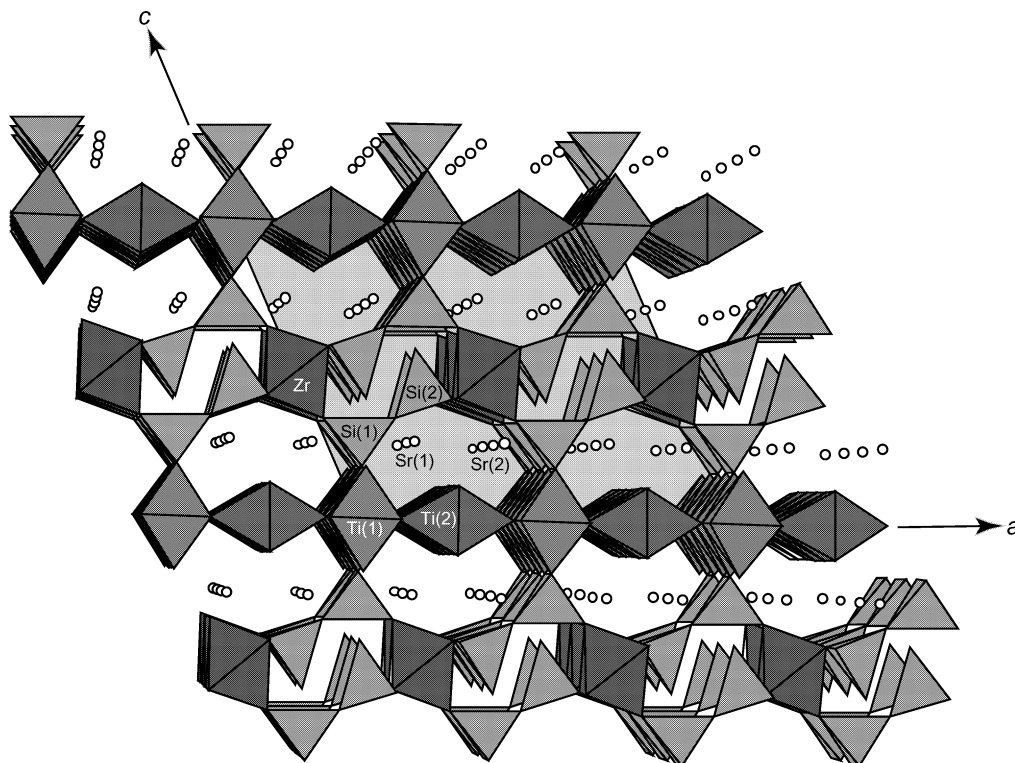
Figure 1. The crystal structure of rengeite, showing the connection of the TiO_6 octahedra (medium gray), ZrO_6 octahedra (dark gray), Si_2O_7 disilicate groups (light gray), and Sr ions (open circles).

perrierite and chevkinite structures.

The true space groups for minerals and synthetic materials in the chevkinite –perrierite group are under discussion. Yang et al. (1991) investigated the space group of chevkinite-(Ce) from China by electron diffraction, and reported that the true space group is $C2/m$, but not $P2_1/a$. They pointed out the possibility of a difference in space group between natural chevkinite-(Ce) and the synthetic La–, Mg–equivalent. These two materials have different chemical compositions and distinct backgrounds of crystallization.

On the other hand, the sample investigated by Gottardi (1960) was recrystallized from a metamict sample by annealing. There is some doubt that the crystal structures of the recrystallized phase and the pre-metamict phase are identical. It is not always possible to determine the true space group with a recrystallized sample or a synthetic analogue.

Several very weak reflections such as $-1,0,-1$; $12,3,-16$; and $0,9,-2$, were observed in the diffraction of rengeite, although they should be absent according to the extinction rule for $C2/m$, $h+k=2n$ present for hkl. Therefore, it was concluded that the true space group for rengeite is $P2_1/a$ (Miyajima et al., 2001). This is compatible with the space group for $La_4Mg_2Ti_3(Si_2O_7)_2O_8$ with the perrierite type structure

(Calvo and Faggiani, 1974). The present study showed that the refinement with space group $C2/m$ gave a better result, i.e., the lower R factors and positive anisotropic displacement parameters for all the sites, than that with space group $P2_1/a$. The deviations of atomic coordinates from the imaginary positions with higher symmetry, which correspond to the atomic coordinates in the $C2/m$ model, are negligible, except for the O(1) site. Consequently, the space group of rengeite can be regarded as pseudo-$C2/m$, though the true space group of rengeite is $P2_1/a$,

The Zr^{4+} ions in rengeite are at the B site, which Fe^{2+} and Mg^{2+} occupy in perrierite-(Ce), but not at the C site in the wall of octahedra. It is worth noting that the crystallo–chemical formula of rengeite was verified as $Sr_4ZrTi_4(Si_2O_7)_2O_8$ in the present structure analysis.

Ito and Arem (1971) suggested that a synthetic analogue of chevkinite-(Ce) is stabilized, relative to that of perrierite-(Ce), by smaller cation in the rare earths site and larger cations in the octahedral sites. The rare earths site is occupied with a larger Sr^{2+} ion in the crystal structure of rengeite. The Zr octahedron in rengeite is slightly larger than the corresponding Fe octahedron in perrierite-(Ce) (Gottardi, 1960), and is significantly smaller than the MgO_6 octahedron in $La_4Mg_2Ti_3(Si_2O_7)_2O_8$ (Calvo and Faggiani, 1974).

The crystal structure of rengeite with the perrierite structure confirms the suggestion on the stabilities of the perrierite and chevkinite structures depending on the ionic radii of cations (Ito and Arem, 1971).

Strontio-chevkinite is a Sr-analogue of chevkinite-(Ce) described by Haggerty and Mariano (1983). They proposed the chemical formula, $(Sr,Ce,Ca)_4(Fe^{2+},Fe^{3+})(Ti,Zr)_2Ti_2Si_4O_{22}$ for strontio-chevkinite based on the ionic radii. They indexed the X-ray diffraction data recorded on Debye-Scherrer films with comparison of diffraction data for chevkinite-(Ce), perrierite-(Ce), Sr-bearing perrierite-(Ce), and synthetic $(Ce_3Sr)Fe(AlTi)Ti_2Si_4O_{22}$. They concluded that their Sr-rich mineral is the Sr-analogue of chevkinite-(Ce), but not the Sr-analogue of perrierite-(Ce). The ionic radius of Sr^{2+} (1.32 Å; Shannon and Prewitt, 1969) is much larger than that of Ce^{3+} (1.14 Å; Shannon and Prewitt, 1969), and sizes of Fe^{2+} and Fe^{3+} ions are almost comparable to that of Ti^{4+} ion. Strontio-chevkinite with larger Sr^{2+} ion in the chevkinite structure contradicts with the relation between the stability of the structures and the radii of cations suggested by Ito and Arem (1971). Although Haggerty and Mariano (1983) indexed the diffraction data based on the chevkinite structure and gave cell parameters as $a=13.56$, $b=5.70$, $c=11.10$Å, $\beta=100.32°$, their X-ray diffraction data of strontio-chevkinite can be indexed by reference to the diffraction data of rengeite, and the lattice parameters, refined with a program written by Toraya (1993), are as follows; $a=13.96(5)$, $b=5.68(2)$, $c=11.94(5)$ Å, $\beta=114.3(3)°$. If strontio-chevkinite is isostructural with perrierite-(Ce), and not with chevkinite-(Ce), and if the crystallo-chemical formula is $(Sr,La,Ce,Ca)_4(Fe,Mg)(Ti,Zr)_2Ti_2(Si_2O_7)_2O_8$, the mineral should be renamed strontio-perrierite-(Ce). It is also probable that Zr atoms occupy the B site instead of the C sites, as well as Zr atoms in rengeite. In this case, the formula of strontio-chevkinite should be $(Sr,La,Ce,Ca)_4Zr(Ti,Fe)_2Ti_2(Si_2O_7)_2O_8$. This means that the material investigated by Haggerty and Mariano (1983) may be an Fe-rich variety of rengeite. A single-crystal study of strontio-chevkinite for the direct observation of cell parameters, especially the β angle, and an analysis of its crystal structure with refinements of site occupancies are required for the resolution of this problem.

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