Structure refinement of high-pressure Ni_2SiO_4 spinel

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Auszug

Die Kristallstruktur des synthetischen Spinells Ni_2SiO_4 wurde bestimmt und bis zu $R = 0,069$ verfeinert. Der Parameter des O-Atoms ist $x = 0,367 \pm 0,003$, die Gitterkonstante des Spinells $a = 8,0424 \pm 0,0002$. Die Si-Atome befinden sich zu 92% in der Punktlage $8a$. Sie sind von den O-Atomen im Abstand von $1,632$ Å tetraedrisch umgeben. Die Punktlage $16d$ ist zu 96% von Ni und zu $4 \pm 3\%$ von Si besetzt. Ihre Umgebung ist oktaedrisch; der Abstand der O-Atome von den Kationen beträgt $2,076$ Å.

Abstract

Integrated x-ray intensities have been measured for 21 reflections in the 2θ range up to $150°$ of polycrystalline Ni_2SiO_4 spinel (a quench product from 40 kbar, 900°C). Using the observed structure factors of these 21 reflections and the least-squares structure refinement computer program of FINGER (1969), refinements were performed on the cation occupancy, the oxygen parameter, three temperature factors and the scale factor. The final R value is 0.069.

In the unit cell of AB_2O_4 spinel (space group $Fd3m$, $Z = 8$), tetrahedrally-coordinated cations occupy equipoint $8a$ and octahedrally-coordinated cations occupy equipoint $16d$; oxygen atoms occupy equipoint $32e$ with coordinates x,x,x. The structure refinement shows that $8\% \pm 6\%$ of the total silicon atoms in Ni_2SiO_4 spinel are octahedrally coordinated. The cation-oxygen bond distance is 1.632 Å in tetrahedral sites (92% Si, 8% Ni), and 2.076 Å in octahedral sites (4% Si, 96% Ni). The refined oxygen parameter, x, is 0.242 ± 0.003, if a center of symmetry is chosen as the origin of coordinates. That parameter transforms to 0.367 ± 0.003, when the tetrahedral site $8a$ is chosen as the origin as is usually done in the literature. The lattice parameter of Ni_2SiO_4 spinel ($a = 8.0424 \pm 0.0002$) used in the structure refinement was determined by least-squares analysis of six high-angle reflections (with semiconductor grade silicon as an internal standard).

Introduction

The spinel structure is face-centered cubic with space group $Fd3m$ (BRAGG, 1915; NISHIKAWA, 1915). The general formula is AB_2O_4, or $A_8B_{16}O_{32}$ per unit cell. In the unit cell, eight tetrahedrally-coordinated

cations occupy equipoint $8a$; sixteen tetrahedrally-coordinated cations occupy equipoint $16d$; and oxygen atoms occupy equipoint $32e$. The positions of cations in equipoints $8a$ and $16d$ are fixed by symmetry, while those of oxygen atoms in equipoint $32e$ are determined by one parameter, x, (*International tables*, Vol. 1, 1969). The spinel structure is also noted for its ability to accommodate the same cations in both tetrahedral and octahedral sites (BARTH and POSNJAK, 1932). As shown rather convincingly by BARTH and POSNJAK, because of the simplicity of the structure, the oxygen parameter and the cation distributions of a particular spinel phase can be satisfactorily refined by x-ray intensities of various reflections obtained by powder diffraction method.

In connection with a phase-equilibrium study of the olivine-spinel transformation in Ni_2SiO_4, a large amount of polycrystalline and essentially pure Ni_2SiO_4 spinel sample was synthesized at high pressures. Silicate spinel is interesting from the standpoint of both oxygen parameter and cation distributions:

1. One would expect that most of the silicon atoms in silicate spinel are tetrahedrally coordinated. Because of the small size of silicon in silicates, the tetrahedral sites in silicate spinel should be much smaller than those in other types of spinels. The value of the oxygen parameter in silicate spinel, which determines the relative size of tetrahedral sites versus octahedral sites, would therefore be drastically different from that of other spinels.

2. Although the silicon atom is always tetrahedrally coordinated in common rock-forming silicates, octahedrally-coordinated silicon is found in some high-pressure silicates, such as stishovite (BAUR and KHAN, 1971). It is therefore quite possible that some silicon atoms are octahedrally-coordinated in silicate spinels.

In addition, the x-ray scattering power of nickel is considerably different from that of silicon. The structure parameters in a nickel-silicate spinel can therefore be refined very precisely using x-ray diffraction procedures. A refinement of both oxygen parameter and cation distributions was therefore carried out on the high-pressure Ni_2SiO_4 spinel based on counter-measured integrated x-ray intensities. The results were included in a Ph. D. thesis (MA, 1972). To the best of my knowledge, this was the first detailed intensity study ever made on a high-pressure silicate-spinel phase.

Recently, YAGI, MARUMO and AKIMOTO (1973) completed a single-crystal structure determination of Ni_2SiO_4 spinel. While their data

confirmed the general features of my results, their data are not in complete agreement with mine in details. For public reference, I present my thesis results in this short article.

Experimental details and results

Sample preparation

A large quantity of polycrystalline Ni_2SiO_4 spinel was synthesized for this study. The starting material was powder of Ni_2SiO_4 olivine (a product of high-temperature sintering, see MA, 1972, 1974), moistened with water. The high-pressure synthesis of Ni_2SiO_4 spinel was made in a large-volume piston (0.75 inch in diameter) cylinder apparatus at the Geophysical Laboratory, Carnegie Institution of Washington, D.C. A single run in a silver capsule (covered, but unsealed) at 40 kbar (nominal pressure), 900 °C for 21.5 hours followed by rapid quenching yielded about 700 mg fine-grained aggregates of an almost pure Ni_2SiO_4 spinel phase except for trace amounts (1—2%) of nickel talc plus NiO.

The sample was crushed and ground under acetone in an agate mortar for more than one hour to reduce the particle size and thus minimize the errors in both the angle and intensity of x-ray reflections caused by possible preferred orientation. The sample holder was made by gluing together two flat sheets of aluminum with a rectangular hole 18 × 10.5 × 0.75 mm drilled through one sheet. The sample was placed and pressed firmly into the hole of the sample holder. The surface of the sample was flattened with the aid of a razor blade.

Instrument description

A Norelco x-ray diffractometer was used to measure data for both lattice parameter and structure refinements. The instrument includes a fine focus copper tube (line focus = 0.04 × 8 mm); a wide-range goniometer (type 150-100-00) equipped with a graphite monochromator that eliminates K_β, fluorescent, and white radiations; a scintillation detector; and the Mark III data control and processor with a pulse-height analyzer set for differential operation to accept 90% of the diffracted beam while avoiding possible instrumental and other external noises. The use of a graphite monochromator and a pulse-height analyzer significantly improves the signal to background ratio, which helps to make a "clean" diffraction pattern and is particularly important for precise intensity measurements of weak reflections.

Lattice parameter refinement

The sample powder was intimately mixed with an equal amount of silicon powder. The silicon powder was prepared from a silicon rod (semiconductor grade, 99.999% Si, less than 0.003 ppm B) which is the same standard material WALDBAUM (1966) used in the study of alkali feldspars. The value 5.43054 Å (PARRISH, 1960) was used as the lattice parameter of silicon.

One forward and one backward scan were made at $0.25°\ 2\theta$ per minute with the chart drive at one inch per minute in the 2θ range 70—145°. The 2θ positions for six high-angle reflections (533, 622, 444, 751, 840, and 844) of Ni_2SiO_4 spinel were read directly from the chart and corrected against four accompanying reflections (331, 422, 531, and 533) of the silicon standard. The corrected 2θ values for these six high-angle reflections were used to refine the lattice parameter of Ni_2SiO_4 spinel in a computer program using least-squares techniques (BURNHAM, 1962). One cycle of refinement yields the parameter 8.0424 ± 0.0002 Å and unit-cell volume 520.18 ± 0.04 Å³.

Intensity measurement

X-ray intensity data for polycrystalline Ni_2SiO_4 spinel were collected using the pulse counting and visual readout systems of the data processor unit associated with the Norelco x-ray diffractometer. According to the space group and cell dimension of Ni_2SiO_4 spinel, 31 reflections are allowed to appear in the 2θ range ($CuK\alpha$ radiation) up to 150°. However, only 28 reflections, including seven that are multiple peaks, have observable intensities (Table 1). The 2θ limit of each peak was first determined for these reflections from chart records. Each peak was then scanned at the rate of $0.25°$ per minute in 2θ. Pulse counts and the elapsed time were continuously registered in the data processor and were read directly from the visual readout window. The background was counted for a fixed time of 20 seconds at each end of the peak. The peak scan was repeated five times; the background was counted ten times for each end, five times before and five times after each peak scan. A total background was computed by multiplying the average background with the average scan time for each peak. The net pulse counts were then obtained for each reflection by subtracting the total background counts from the average total peak counts.

Table 1 shows the net pulse counts and relative intensities for these reflections completed at three separate periods of measurement.

During each measurement, the 311 peak was scanned every two or three hours to check for electronic fluctuations. The fluctuations were usually small and can be ignored during each period of measurement, but the total pulse counts for the same reflections varies substantially among separate periods of measurement. The relative intensities as shown in Table 1 for the same reflections measured in two different

Table 1. *X-ray powder diffraction intensity data for* Ni_2SiO_4 *spinel*

hkl	Net pulse counts (Measurement period)			$(I_{hkl}/I_{311}) \times 100\%$ (Measurement period)		
	1	2	3	1	2	3
111	54,795	—	—	26.3	—	—
220	19,861	—	—	9.5	—	—
311	208,361	194,610	126,560	100.0	100.0	100.0
222	17,732	—	—	8.5	—	—
400	110,459	106,152	—	53.0	54.55	—
331	21,441	20,381	—	10.29	10.47	—
422	6,943	6,298	—	3.3	3.2	—
511, 333	—	48,032	—	—	24.68	—
440	90,941	—	—	43.65	—	—
531	6,171	—	—	2.96	—	—
442*	—	—	—	—	—	—
620	2,421	—	—	1.16	—	—
533	13,693	—	—	6.57	—	—
622	7,254	—	—	3.48	—	—
444	9,687	—	—	4.65	—	—
711, 551	—	2,758	—	—	1.4	—
642	—	3,670	—	—	1.89	—
731, 553	—	28,223	—	—	14.5	—
800	—	11,131	—	—	5.7	—
733	—	1,418	—	—	0.7	—
644*	—	—	—	—	—	—
822, 660	—	1,731	—	—	0.89	—
751, 555	—	13,503	—	—	6.9	—
662	—	3,587	—	—	1.8	—
840	—	9,113	—	—	4.68	—
911, 753	—	1,773	—	—	0.9	—
842*	—	—	—	—	—	—
664	—	—	424	—	—	0.3
931	—	8,950	—	—	4.6	—
844	—	38,630	—	—	19.85	—
933, 771, 755	—	2,462	—	—	1.27	—

* Having intensity less than the minimum observable intensity.

periods, however, remain more or less constant. For reflections having more than one value of relative intensity, the value from first determination is used for the structure refinement.

Structure refinement

Excluding seven reflections that are multiple peaks, 24 reflections of those listed in Table 1 were used for the structure refinement. Among them, only 21 reflections have observable intensities. The relative integrated intensities, I, of these 21 reflections were reduced to observed structure factors (also on a relative basis), F_o, according to the following equation (BUERGER, 1960; AZAROFF, 1968):

$$F_o = \sqrt{I/(\overline{MLp})}$$

M: multiplicity factor

L,p: Lorentz and polarization factors modified for the use of a monochromator, $Lp = (1 + \cos^2 2\alpha \cos^2 2\theta)/(\sin 2\theta \sin \theta)$ in which $\alpha =$ the Bragg angle of the graphite monochromator; $2\alpha = 26°18'$ (for Cu$K\alpha$). The absorption correction is not included in this equation because it is independent of θ (KLUG and ALEXANDER, 1954) and thus remains as a constant for all reflections if we assume the thickness of powder mount (0.75 mm) is large enough to give maximum diffracted intensities. Extinction correction is also ignored.

For atoms involved in the structure refinement, the x-ray scattering factors are available from the literature, but the average scattering factors for the cation sites are dependent on the cation occupancy. Furthermore, the x coordinate of oxygen atoms in the spinel structure is variable. There are, therefore, six variable parameters (the cation occupancy, the oxygen parameter, the scale factor and three isotropic temperature factors) associated with each of the observed structure factors. The structure refinement was thus simply a process of finding the best values for six parameters to fit these observed structure factors.

This process was carried out in RFINE, a Fortran IV computer program of FINGER (1969), using the technique of full-matrix least-squares refinement. Analytic approximations of Hartree-Fock scattering factors of O^{-1}, Ni^{+2} and Si^{+4} (CROMER and MANN, 1968) were used without anomalous dispersion corrections. Unit weight was assumed for all reflections.

Table 2. *Results of structure refinement of* Ni_2SiO_4 *spinel*
Standard errors are in parentheses and refer to same decimal level

Atom	Parameter	First refinement		Second refinement	
		Initial	Final	Initial	Final
	Scale factor	0.30	0.34(1)	0.34	0.34(1)
O (32e)	x	0.385	0.367(3)	0.367	0.367(3)
	B	0.5	0.3(4)	0.5	$0.2(4)\,Å^2$
M (16d)	Occupancy Ni	1.0	0.96(3)	0.50	0.96(3)
	Si	0.0	0.04	0.50	0.04
	B	0.5	1.9(2)	0.5	$1.9(2)\,Å^2$
T (8a)	Occupancy Ni	0.0	0.08	1.0	0.08
	Si	1.0	0.92	0.0	0.92
	B	0.5	0.7(6)	0.5	$0.6(6)\,Å^2$

Two separate refinements using different initial values for both cation occupancy and oxygen parameter were made to check the results. The first refinement involved 24 reflections including three that have intensities less than the minimum observable intensity. The second refinement was made without these three reflections. Three cycles of RFINE were required for the first refinement; whereas four cycles of RFINE were required for the second refinement to reach convergence. The final R value is 0.069 for both refinements which is computed from unrejected reflections using the formula $R^2 = \Sigma(|F_o| - |F_c|)^2/\Sigma |F_o|^2$. Table 2 contains the initial values and refined parameters with standard errors from both refinements. Table 3 lists the principal bond-lengths.

The structure refinement was carried out assuming the center of symmetry as the origin of coordinates. The results show that Ni_2SiO_4 spinel has an oxygen parameter $x = 0.242 \pm 0.003$. It transforms to 0.367 ± 0.003 if a tetrahedral site, $8a$, is chosen as the origin of coordinates as is usually done in the literature. The latter value is listed in Table 2 and is used for the discussion in the following section.

Discussion

The initial values used for the first refinement in Table 2 assumed a normal spinel cation occupancy (*i.e.*, the tetrahedral sites are completely occupied by silicon atoms); 0.385 for the oxygen parameter

Table 3. *Bond lengths in* Ni_2SiO_4 *spinel*

	First refinement	Second refinement	Average
Tetrahedron			
(4)* T—O	1.636 Å	1.628 Å	1.632 Å
(6) O—O	2.671	2.658	2.665
Octahedron			
(6) M—O	2.073	2.078	2.076
(6) O—O (shared edge)	3.016	3.028	3.022
(6) O—O (unshared edge)	2.846	2.846	2.846
Cation-cation distances			
T—T	3.482	3.482	3.482
T—M	3.334	3.334	3.334
M—M	2.843	2.843	2.843

* Multiplicity.

($>$ 0.375 which is the value for ideal cubic closest packing). For the second refinement they were, instead, those corresponding to the inverse structure (*i.e.*, tetrahedral sites are completely occupied by nickel atoms); and $x = 0.367$ (< 0.375). With such drastically different initial values, these two separate refinements have nevertheless reached similar results as shown in Table 2. Furthermore, the correlation matrices in both refinements showed that all six parameters are essentially independent of each other except for a moderate interdependence between the cation occupancy and temperature factor in tetrahedral sites $8\,a$. These indicate that RFINE works satisfactorily for the refinement of Ni_2SiO_4 spinel structure. However, the refinement of temperature factors appears to be less satisfactory than the refinement of other parameters. A uniform initial value 0.50 was used for all three temperature factors in both refinements. But the refined temperature factors for atomic sites $32\,e$ and $8\,a$ have huge standard errors, while the temperature factor for atomic sites $16\,d$ is 1.9, a value much larger than usually expected.

Ni_2SiO_4 spinel has an oxygen parameter $x = 0.367 \pm 0.003$. Since x is less than 0.375, the tetrahedral sites $8\,a$ are smaller and the octahedral sites $16\,d$ are larger than those in the ideal cubic closest-packed structure. A consequence of this arrangement is that the unshared edges of the coordination polyhedra of oxygen atoms about the

octahedral site are shorter (2.85 Å) than the shared edges (3.02 Å, Table 3). This violates Pauling's rule for edge sharing. The situation is complete opposite for most spinels that crystallize at one atmosphere. For such ordinary spinels, x lies in the range 0.380 to 0.390 (BLASSE, 1964; WYCKOFF, 1965) which corresponds, instead, to smaller octahedral sites and shorter shared edges of the octahedral oxygen polyhedra in comparison to those in an ideal cubic closest packing of oxygen atoms. KAMB (1968) has suggested earlier that the peculiarity of silicate spinels in this respect would account for the reason why they can not form at atmospheric pressure as stable phases.

The refinement of cation occupancy showed that $8\% \pm 6\%$ of the total silicon atoms are octahedrally coordinated by oxygen (or $4\% \pm 3\%$ of the total nickel atoms are tetrahedrally coordinated). However, the T—O bond lengths (1.632 Å) and M—O bond lengths (2.076 Å) are both comparable to the corresponding mean bond lengths Si—O (1.640 Å) and Ni—O (2.089 Å) in Ni_2SiO_4 olivine (BROWN, 1970). The T—O bond length is also in close agreement with the mean Si—O bond length (1.638 Å) in other silicates with four-coordinated silicon atoms (BROWN and GIBBS, 1969). The conclusion is therefore that the amount of octahedral silicon in Ni_2SiO_4 spinel is either insignificant or too little to cause the change of bond length to any appreciable degree.

YAGI et al. (1973) recently completed a single-crystal structure determination on crystals of Ni_2SiO_4 spinel synthesized at 55 kbar, 1400 °C. They stated that only $0.5\% \pm 1.2\%$ of the total silicon atoms are octahedrally coordinated. But the raw data listed in their Table 1 indicate that $1.0\% \pm 0.6\%$ of the octahedral site are occupied by silicon atoms. Since the octahedrally-coordinated sites in the spinel structure are twice as many as the tetrahedrally-coordinated ones, their data really imply that $2.0\% \pm 1.2\%$ of the total silicon atoms are octahedrally coordinated. Their results are listed below along with the corresponding results obtained from my thesis research:

	YAGI et al. (1973)	MA (1972)
Lattice parameter	8.044 ± 0.001 Å	8.0424 ± 0.0002 Å
Oxygen parameter	0.3687 ± 0.0002	0.367 ± 0.003
T—O bond length	1.654 Å	1.632 Å
M—O bond length	2.063 Å	2.076 Å
Octahedrally-coordinated silicon atoms	$2.0\% \pm 1.2\%$	$8\% \pm 6\%$

The lattice parameter they used was obtained from single-crystal data and is probably less precise than the one used in this study. A larger lattice parameter combined with a larger oxygen parameter give rise to an average T—O bond length in their data considerably bigger than the one obtained from this study. As for the cation distributions, the results show that their sample is practically a normal spinel (*i.e.*, essentially all silicon atoms are tetrahedrally coordinated), while my sample appear to indicate that a small amount of silicon atoms are possibly octahedrally coordinated.

Among divalent Fe, Co, and Ni ions, Ni^{+2} possesses the largest octahedral site-preference energy (McClure, 1965). If some silicon atoms are indeed octahedrally coordinated in Ni_2SiO_4 spinel, one may expect to find more octahedrally-coordinated silicon atoms in Fe_2SiO_4 and Co_2SiO_4 spinels. It is rather surprising that recent data seem to indicate that Fe_2SiO_4 spinel (Yagi *et al.*, 1973) and Co_2SiO_4 spinel (Morimoto, private communication, 1973) are both practically normal spinels.

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