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Thermal Expansion of γ-Ni_2SiO_4 Spinel

By

Masahiro OSAKO

Department of Science and Engineering, National Science Museum,
3–23–1 Hyakunincho, Shinjuku-ku, Tokyo 169, Japan

Abstract

Thermal expansion of γ-Ni_2SiO_4 spinel has been measured by X-ray diffraction method in a temperature range from 297 K to 1027 K under vacuum condition. Gamma Ni_2SiO_4 has a lattice parameter of 804.43 pm at 297 K. The volume thermal expansion of the spinel is determined to be $2.06 \times 10^5\,K^{-1}$ at 300 K and $2.33 \times 10^{-5}\,K^{-1}$ at 700 K. The lattice parameter of γ-Ni_2SiO_4 spinel is reversible over a heating cycle unlike γ-Fe_2SiO_4 which shows a contraction.

1. Introduction

Silicate spinels have attracted interest in the earth science field because they are considered to be the most abundant structure in the earth's transition zone beginning at the 400 km depth and ending at the 700 km depth. The candidate mineral in the earth's transition zone is most likely to be a solid solution of magnesium and iron bearing silicate spinel group, namely β, γ-$(Mg, Fe)_2SiO_4$, however, other silicate spinels such as γ-Co_2SiO_4 and γ-Ni_2SiO_4 have also been studied in order to compare physical properties and crystallographic characterization with the Mg–Fe bearing silicate spinel.

Gamma Fe_2SiO_4 reveals anomalous thermal expansion (YAMANAKA, 1986; MING *et al.*, 1987), and irreversible change of the lattice dimension during the heating cycle (YAMANAKA, 1986; OSAKO, 1986). YAMANAKA (1986) also reported that γ-Ni_2SiO_4 spinel also has an irreversible change of lattice dimension during heating resulting in a contraction of the lattice parameter. This short note reports the thermal expansion of γ-Ni_2SiO_4 spinel from measurements of the lattice parameter temperatures up to 727°C.

2. Experimental

The sample was synthesized in a tetrahedral anvil high-pressure apparatus at the Institute for Solid State Physics, University of Tokyo. The spinel phase of Ni_2SiO_4 was converted from the olivine phase, and recovered into the ambient condition by quenching method.

The lattice parameter of the cubic structure was measured by the Debye-Scherrer method using a high-temperature X-ray powder camera (Rigaku 1211B2). The powdered sample of 0.05 mg was adhered as a thin layer (0.03 mm or 0.05 mm) on a

platinum (99.99% purity) wire (OSAKO, 1986; HAMANO, 1989), and placed in a small furnace which an inhomogeneous temperature distribution because of the windows required for the X-ray path. No K_β filter was installed on a X-ray source because K_β radiation was required to obtain more diffracted lines in high diffraction angles. The wire covered with the sample was heated at 520°C in vacuum to release strain in the platinum wire and to evaporate the petroleum component of the adhesive. The camera body was evacuated to eliminate scattering of X-rays from air. The exposure time of the X-ray film was 45 to 50 minutes at a power of 40 kV × 35 mA using Cr–K radiation.

To determine the lattice parameter of the cubic γ-Ni_2SiO_4 spinel, the angles of the five diffraction lines produced by Cr radiation, (533) and (444) for both $K_{\alpha 1}$ and $K_{\alpha 2}$, (622) for $K_{\alpha 1}$, and only at the highest temperature (533) line for K_β, were measured within 0.007° by means of a travelling microscope. The lattice parameter was calculated by extrapolating to $\theta = 90°$ by the least square method (COHEN, 1935), where θ is diffraction angle. In this calculated $\cos^2\theta$ was adopted to a extrapolation function where the systematic error of the lattice parameter vanished.

The temperature of the sample was measured to ±3 K from the lattice parameter of the platinum wire. The recommended values for thermal expansion of platinum (TOULOUKIAN *et al.*, 1976) were used. A thermocouple installed near the sample was used for controlling and monitoring temperature of the furnace.

Three runs were performed for lattice parameter measurement. Run 1 had a single exposure at room temperature, 25°C. Run 2 and Run 3 consisted of 8 exposure: beginning and ending with measurements at room temperature with the six other measurements at elevated temperatures.

3. Results

The results of the lattice parameter measurements are summarized in Table 1 and shown in Figure 1. The temperature of the sample is determined from the lattice parameter of the platinum with reference to a fixed value of 392.37 pm at 297 K.

In the Run 2 both the lattice parameters of the platinum wire and the sample have slightly elongated value at the beginning and at the end of the measurements. This was probably due to a small movement of the film from regular position in the film cassette around the window for X-ray inlet at $\theta = 90°$. To account for this the lattice parameter of platinum, 392.44 pm at 297 K is adopted as a reference for temperature measurement for Run 2. The lattice parameter of the spinel sample was obtained by a procedure of multiplying lattice parameter, 804.43 pm at 297 K by the relative change of the parameter with reference to the value, 804.52 pm at the beginning of the Run 2.

In Table 2 the lattice parameter and the volume thermal expansion of γ-Ni_2SiO_4 spinel is listed. The lattice parameter, a_0 is fitted for a polynomial of the third order by the least square method, as $a_0 = (802.78 + 5.585 \times 10^{-3} T - 5.256 \times 10^{-7} T^2 + 9.71 \times 10^{-10} T^3)$ pm, where T is the absolute temperature. This fitting is shown in the curve in Figure 1. The thermal expansion of γ-Ni_2SiO_4 spinel is smaller than the other silicate

Table 1. Lattice parameter measurement of γ-Ni_2SiO_4 and platinum

The second column of the lattice parameter of γ-Ni_2SiO_4 for the run 2 shows the reduced value with reference to that of 804.43 pm at 297 K.

	Lattice parameter (pm)			Temperature (K) with reference to the lattice parameter of 392.44 pm (for Run 1) 392.37 pm (for Run 2)
	platinum	γ-Ni_2SiO_4		
		measured	reduced	
Run 1	392.36 (0)	804.43 (4)		298 (25°C)
Run 2	392.43 (1)	804.52 (1)		297 (24°C)
	392.72 (1)	804.93 (3)	804.84	374
	392.92 (1)	805.26 (3)	805.17	429
	393.15 (1)	805.60 (2)	805.51	491
	393.36 (1)	805.94 (2)	805.85	547
	393.57 (1)	806.27 (4)	806.18	603
	393.78 (1)	806.61 (2)	806.52	658
	392.44 (1)	804.50 (2)		297 (24°C)
Run 3	392.40 (1)	804.43 (2)		297 (24°C)
	393.92 (1)	806.77 (3)		712
	394.16 (1)	807.22 (4)		773
	394.38 (1)	807.65 (2)		828
	394.62 (1)	808.01 (2)		887
	394.89 (1)	808.45 (2)		952
	395.21 (1)	809.01 (2)		1027
	392.37 (1)	804.40 (2)		297 (24°C)

Figures in parentheses represent the probability error.

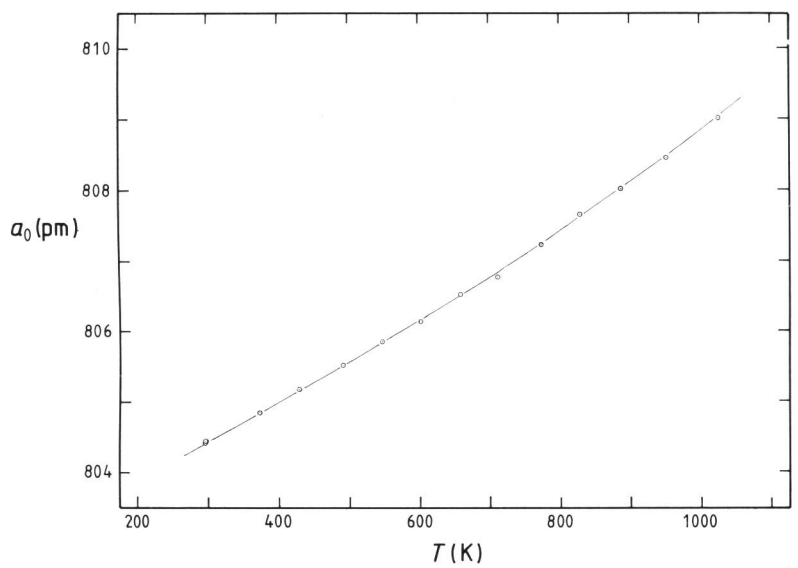

Figure 1. Lattice parameter (a_0) of γ-Ni_2SiO_4 versus temperature (T). Measurement uncertainties are within the extent of the circle.

Table 2. Lattice parameter (a_0) and volume thermal expansion (α_v) of γ-Ni_2SiO_4 at selected temperatures (T)

T (K)	300	400	500	600	700	800	900	1000
a_0 (pm)	804.44	804.99	805.56	806.15	806.77	807.41	808.09	808.81
α_v ($10^{-5}K^{-1}$)	2.06	2.10	2.16	2.23	2.33	2.46	2.60	2.76

spinels, γ-Mg_2SiO_4 (SUZUKI, 1978) or γ-Fe_2SiO_4 (MAO *et al.*, 1969) at elevated temperatures.

YAMANAKA (1986) reported that the lattice dimension of γ-Ni_2SiO_4 spinel had undergone contraction by heating up to 700°C or 800°C. Consequently, the lattice parameter changed anomalously with temperature on heating procedure. Moreover, irreversible change of lattice parameter by heating was observed in γ-Fe_2SiO_4 spinel (YAMANAKA, 1986; OSAKO, 1986), and in γ-$(Mg, Fe)_2SiO_4$ spinel (MING *et al.*, 1987). In this measurement, however, the change in the lattice parameter of γ-Ni_2SiO_4 spinel reveals reversible upon heating cycle, and no contracting of the lattice dimension was observed at least up to 730°C for 50 minutes, the time required for adequate exposure of X-ray patterns on a film.

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References

COHEN, M. U., 1935. Precision lattice constants from X-ray powder photographs. *Rev. Sci. Instr.*, 6: 68–74.

HAMANO, Y., 1989. Lattice constants of titanomagnetites at high temperatures. *J. Jeomag. Geoelectr.*, 41: 65–75.

MAO, H. K., T. TAKAHASHI, W. A. BASSETT, J. S. WEAVER and S. AKIMOTO, 1969. Effect of temperature and pressure on the molar volumes of wüstite and of three $(Fe, Mg)_2SiO_4$ spinel solid solutions. *J. Geophys. Res.*, 74: 1061–1069.

MING, L. C., M. H. MANGHNANI, Y. H. KIM and S. USHA-DEVI, 1987. Thermal expansivity of γ-Mg_2SiO_4 and γ-$(Mg, Fe)_2SiO_4$ spinels to 900°C using synchrotron radiation. *Transact. Am. Geophys. Uni.*, 68: 409.

OSAKO, M., 1986. Anomalous thermal expansion of Fe_2SiO_4 spinel. *Bull. Natn. Sci. Mus., Tokyo, Ser. E*, 9: 1–4.

SUZUKI, I., E. OHTANI and M. KUMAZAWA, 1979. Thermal expansion of γ-Mg_2SiO_4. *J. Phys. Earth*, 27: 53–61.

TOULOUKIAN, Y. S., R. K. KIBBY, R. E. TAYLOR and P. D. DESAI, 1976. Thermal expansion: Metallic elements and alloys (Thermophysical properties of matter, Vol. 12), 1348 pp., IFI/Plenum, New York–Washington.

YAMANAKA, T., 1986. Crystal structure of Ni_2SiO_4 and Fe_2SiO_4 as a function of temperature and heating Duration. *Phys. Chem. Minerals*, 13: 227–232.