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Anomalous Thermal Expansion of Fe_2SiO_4 Spinel

By

Masahiro OSAKO

Department of Physical Sciences, National Science Museum, Tokyo

Abstract The lattice parameter of γ-Fe_2SiO_4 spinel was measured by the Debye-Scherrer method from 290K to 680K. An anomalous change of the lattice dimension was found during heating up to 470K and annealing reduced the dimension to a settled value, which means that the lattice dimensions of quenched high pressure minerals might show unexpected variation depending on the cooling rate. The mean volume thermal expansion of γ-Fe_2SiO_4 in the temperature range investigated is $(2.5\pm0.1)\times 10^{-5}K^{-1}$.

1. Introduction

Orthosilicate spinels have attracted wide attention because olivine is thought to be the most abundant mineral in the earth's upper mantle and is predicted to transform into the spinel structure or the momefied spinel structure in the transition zone of the mantle. Measurements of thrmal expansion of mantle minerals are indispensable because the data are vital to the equation of state of the earth's interior. The thermal expansion of γ-Mg_2SiO_4, the principal silicate spinel in the mantle, was given by Suzuki *et al.* (1979). Another important end member, γ-Fe_2SiO_4 was investigated earlier than γ-Mg_2SiO_4, however, the thermal expansion was insufficiently determined.

Recently Yagi and Akimoto (1985) suggested that the thermal expansion data of quenched minerals under metastable conditions are dengerous to apply them to the earth's interior. Their suggestion is based on a comparison of in-situ high pressure observations of volume changes using synchrotron radiation with those at atmospheric pressure. Some extraordinary behavior of lattice dimensions could have seen on quenched mantle minerals held under metastable conditions.

2. Experimental

The polycrystalline γ-Fe_2SiO_4 spinel was synthesized at high pressure and high temperature in a tetrahedral anvil apparatus at the Institute for Solid State Physics, University of Tokyo. A high temperature Debye-Scherrer camera (RIGAKU 1211B2) was used for the thermal expansion measurement. The powdered sample of 0.05 mg to 0.1 mg was pasted thinly on a pure (99.99%) platinum wire, 0.2 mm in diameter, with petrorem product, so that the x-ray differaction patterns both from the sample and from the wire have same intensities on a film. This permits the use of Pt as

internal standard for the temperature. Since both $K\alpha$ and $K\beta$ radiations are required for platinum and $K\alpha$ radiation for the spinel sample, no filter inserted. The camera body was evacuated to eliminate scattering of x-rays due to air and prevent the sample from oxidation. The exposure time was 40 minutes for a power of 40 kV$\times$35 mA.

To determine the lattice parameter of the cubic spinel the angles of the (533) and (444) diffraction lines produced by Cr $K\alpha_1$ and $K\alpha_2$ were measured within 0.007° by means of a travelling microscope. The temperatures were determined to $\pm$3K from the lattce parameter of platinum. The recommended values for thermal expansion of platinum (Touloukian *et al.*, 1976) were used.

3. Results and discussion

Two specimens of spinel were prepared from the same badge: one of these (Specimen I) was employed for thermal expansivity measurements, and the other (Specimen II) was used for checking. The measurements were started at room temperature, and made at intervals of 50K to 70K. The heating rate, in each interval between exposures, was set at 10K/min; the total run was completed in 280 minutes. The diffraction pattern of the spinel was clearly observed up to 683K, the highest temperature.

It is a remarkble result that a nonlinear thermal expansion appeared in the low temperature range from 300K to 470K (Fig. 1 and Table 1). The pattern of the spinel could not observed after cooling to room temperature, and there is no indication of reversibility of the thermal expansivity of the spinel phase. The lattice parameter at 291K of Specimen II was determined as $(8.2389\pm0.0008)\times10^{-10}$ m after annealing at 600K for 30 min. This value, considerably larger than that of $(8.234\pm0.001)\times10^{-10}$ m by Yagi *et al.* (1974), is different from that of Specimen I before heating, however, it lies on the line extrapolated form the higher temperatures for Specimen I in the region where the lattice parameter changes linearly with temperature. One thus comes to the conslusion that the nonlinear change in the lattice parameter of this spinel sample is irreversible and that, most probably, annealing reduces the lattice parameter to a settled value. The mean volume thermal expansion of γ-Fe_2SiO_4 spinele between 300K and 700K is $(2.5\pm0.1)\times10^{-5}K^{-1}$ from the lattice parameters of Specimen I measured at high temperatures with reference to the lattice parameter at 291K measured on Specimen II after annealing at 600K. This value is consistent with a previous one by Mao *et al.* (1969).

An irreversible change of lattice parameter of quenched high pressure mineral was also found on Ni_2SiO_4 spinel (Yamanaka, 1986). In his experiment γ-Ni_2SiO_4 experienced a drastically contraction of lattice parameter during heating for several hours at 700°C and 800°C (while γ-Fe_2SiO_4 exhibited a abrupt increase of lattice parameter above 400°C). Although the temperature ranges and the heating durations are different, it is likely that the decreasing of latttice parameter for γ-Ni_2SiO_4 during heating is similar phenomenon for γ-Fe_2SiO_4 in this study.

Mantle minerals obtained by temperature quenching at high pressure following

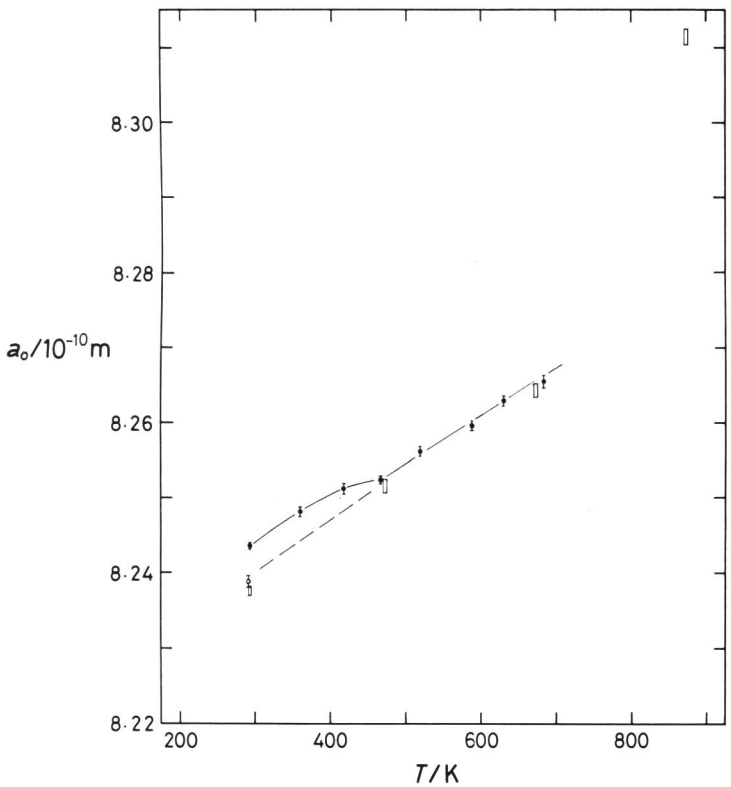

Fig. 1. Lattice parameter (a_0) of γ-Fe_2SiO_4 as a function of temperature (T) (closed circles). As the temperature is increasing, anomalous change of the lattice parameter of the spinel is observed up to 470K, An open circle indicates the parameter after annealing. The mean volume thermal expansion of γ-Fe_2SiO_4 between 300K and 700K is $(2.5\pm0.1)\times10^{-5}K^{-1}$. Open quadrangles are referred to the results by Yamanaka (1986).

Table 1. Lattice parameters of γ-Fe_2SiO_4 at several temperatures.
Parenthesized figures represent probability errors of least unit cited. The uncertainty of the temperatures is ±3K.

T/K	293	360	418	466	520
$a_0/10^{-10}$ m	8.2432(3)	8.2481(6)	8.2512(7)	8.2523(5)	8.2563(7)

T/K	587	629	683	291
$a_0/10^{-10}$ m	8.2596(5)	8.2629(6)	8.2654(8)	*8.2389(8)

* After annealing at 600K for 30 min.

high temperature-high pressure synthesis might remain in an expanded state, i.e. deviate from the heating curve of volume chnge, at some point during cooling. The cooling rates are usually very fast and not controlled in recovering the samples of high pressure phases, therefore, the lattice dimensions of those minerals could have unexpected variations.

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