

Enstatite, $\text{Mg}_2\text{Si}_2\text{O}_6$: A neutron diffraction refinement of the crystal structure and a rigid-body analysis of the thermal vibration

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Abstract. Synthetic enstatite, $\text{Mg}_2\text{Si}_2\text{O}_6$, is orthorhombic, space group *Pbca*, with eight formula units per cell and lattice parameters $a = 18.235(3)$, $b = 8.818(1)$, $c = 5.179(1)$ Å at 23°C. A least-squares structure refinement based on 1790 neutron intensity data converged with an agreement factor $R(F^2) = 0.032$, yielding Mg–O and Si–O bond lengths with standard deviations of 0.0007 and 0.0008 Å, respectively. The variations observed in the Si–O bond lengths within the silicate tetrahedra *A* and *B* are caused by the differences in primary coordination of the oxygen atoms and the proximity of the magnesium ions to the silicon atoms. The latter effect is most pronounced for the bridging bonds of tetrahedron *A*. The smallest O–Si–O angle is the result of edge-sharing by the Mg(2) octahedron and the *A* tetrahedron. An analysis of rigid-body thermal vibrations of the two crystallographically independent $[\text{SiO}_4]$ tetrahedra indicates considerable librational motion, leading to a thermal correction of apparent Si–O bond lengths as large as +0.002 Å at room temperature.

Introduction

Enstatite is the magnesium end-member $\text{Mg}_2\text{Si}_2\text{O}_6$ of orthopyroxenes $(\text{Mg,Fe})_2\text{Si}_2\text{O}_6$. It is a rock-forming silicate occurring in terrestrial and lunar rocks and meteorites and is considered to be an important constituent of the earth's upper mantle. Because of its geophysical importance, we have chosen it for detailed structural and lattice dynamical studies on the effects of pressure and temperature on pyroxene minerals. The enstatite structure has been refined by a number of workers using X-ray diffraction data measured under ambient laboratory pressure and temperature (Morimoto and Koto, 1969; Ghose and Wan, 1976; Hawthorne and Ito, 1977; Ghose, Wan, Ralph and McMullan, 1980; Sasaki, Fujino, Takéuchi and Sadanaga, 1980; Sasaki, Takéuchi, Fujino and Akimoto, 1982; Ohashi, 1984), as well as at 21 kbar (Ghose, et al., 1980) and (on $\text{Mg}_{0.3}\text{Fe}_{0.7}\text{SiO}_3$) up to 850°C (Smyth, 1973). We present here the results of a neutron diffraction study under ambient conditions, undertaken to obtain accurate positional and thermal vibration parameters that are unbiased by aspherical bonding electron densities of the atoms. We also present an analysis of the configurational differences in the silicate and magnesium polyhedra, together with an analysis of the rigid-body motion of the individual silicate tetrahedra of the single silicate chains. Neutron studies on two other pyroxenes, diopside, $\text{CaMgSi}_2\text{O}_6$, and spodumene, $\text{LiAlSi}_2\text{O}_6$, have been completed (Ghose and Busing, 1984).

Experimental

Crystals of orthoenstatite, $\text{Mg}_2\text{Si}_2\text{O}_6$, were obtained by the primary crystallization in the system $\text{MgO} - \text{SiO}_2 - \text{lithium vanadomolybdate}$ (Ito, 1975). Slow cooling (~ 1.5 deg/h) of the melt from 930°C to 650°C yielded prismatic crystals with [001] elongation, exhibiting forms $\{100\}$, $\{210\}$, and $\{011\}$. The reported composition is essentially MgSiO_3 , with 0.17 wt% Li_2O and 0.27 wt% V_2O_5 . The crystal selected for study (Table 1) was mounted within a few degrees of the c axis. Diffraction data were collected at room temperature on a 4-circle diffractometer at the Brookhaven High Flux Beam Reactor. The neutron beam, monochromatized by reflection from the 002 planes of a beryllium crystal, was of wavelength $1.0024(1)$ Å based on KBr ($a_0 = 6.6000$ Å at 25°C).

The unit-cell parameters (Table 1) were determined by a least-squares fit of $\sin^2\theta$ values for 32 reflections distributed over the reciprocal lattice in the range $45^\circ < 2\theta < 57^\circ$. Intensity data were recorded for reflections $(+h, +k, +l; \sin\theta/\lambda \leq 0.80 \text{ \AA}^{-1})$ using $\theta/2\theta$ step scans over scan ranges $\Delta(2\theta) = 3.0^\circ$ for $0^\circ < 2\theta < 65^\circ$ and $\Delta(2\theta) = 2.38 + 2.52 \tan\theta$, for $65^\circ < 2\theta < 107^\circ$. Between 60 and 88 points were sampled on the scan profiles, with counting time at each point (~ 2 s) being determined by a fixed

