Single-crystal compression and crystal structure of clinopyroxene up to 10 GPa

LI ZHANG, HANS AHBSBAHS, STEFAN S. HAFNER, AND ALI KUTOGLU

Scientific Center of Materials Sciences and Institute of Mineralogy, University of Marburg, 35032 Marburg, Germany

ABSTRACT

The hydrostatic compression of synthetic single crystals of diopside, CaMgSi₂O₆, and hedenbergite, CaFeSi₂O₆, was studied at 33 pressures up to 10 GPa by X-ray diffraction. In addition, intensity data for hedenbergite were collected at 12 pressures up to 10 GPa. For determination of the elasticity two crystals were loaded together in a diamond cell. The axial compressibilities \( b_a \), \( b_b \), and \( b_c \) of diopside and hedenbergite are 2.36(4), 3.17(4), and 2.50(4) \( \times 10^{-2} \) GPa\(^{-1} \), and 1.93(5), 3.38(6), and 2.42(8) \( \times 10^{-2} \) GPa\(^{-1} \), respectively. The bulk moduli \( (K_V) \) and their pressure derivatives \( (\overline{K_V}) \) were determined simultaneously from a weighted linear fit of a third order Birch-Murnaghan equation of state to the volume data at elevated pressures. \( K_V \) and \( \overline{K_V} \) are 104.1(9) GPa and 6.2(3) for diopside and 117(1) GPa and 4.3(4) for hedenbergite, respectively.

The unit-cell parameters decrease continuously with pressure. The larger polyhedra show more compression than the smaller ones. Between 0.1 MPa and 10 GPa the polyhedral volumes of CaO₈, FeO₆, and SiO₄ decrease by 8.4, 6.6, and 2.9%, respectively. The longest bonds of CaO₈ and FeO₆ show most compression. Significant compression in the two shortest Si-O1 and Si-O2 bond lengths of the SiO₄ tetrahedra was observed at relatively low pressures, resulting in a tetrahedral volume compression of 1.6% between 0.1 GPa and 4 GPa and 1.3% between 4 and 10 GPa. The compression of the unit cell can be described by the volume compression of the individual CaO₈ and FeO₆ polyhedra, with the SiO₄ tetrahedron playing a minor role. Diopside is more compressible than hedenbergite as shown by their axial and volume compressibilities because the FeO₆ octahedron is significantly more rigid than MgO₆ at high pressures. This observation implies that octahedrally coordinated Fe²⁺ behaves differently from Mg at high pressures, in contrast to their behavior at ambient conditions.

INTRODUCTION

Ca-rich clinopyroxenes are regarded as major minerals of the mantle models and they have been the subject of several recent studies (Levien et al. 1979; Levien and Prewitt 1981; Kandelin and Weidner 1988; Zhang et al. 1989; Zhang and Hafner 1992; Comodi et al. 1995). For example, significant amounts of Ca-rich clinopyroxenes are accounted for in both the pyrolite (Ringwood 1975) and piclogite (Anderson and Bass 1984) models, with a volume fraction ranging from about 10–40% in the upper mantle. One way to constrain these models tightly is to compare seismic velocities directly with sound velocities measured on mantle minerals in the laboratory under mantle pressures (Zhang and Chopelas 1994). To accomplish this, data are needed for precise determination of equations of state at high pressures.

Ca-rich clinopyroxenes have monoclinic symmetry (space group \( \text{C}2/c \)). Because of their low symmetry, it is not easy to obtain precise crystal structure data using high-pressure techniques on polycrystalline samples because of coincidence of equivalent reflections and accidental overlap of nonequivalent reflections. Data now available were obtained mainly from single crystal diffraction at high pressures (Levien and Prewitt 1981; Comodi et al. 1995). Because those experiments were limited to pressures up to about 5 GPa, it is necessary to measure data at higher pressures, considering the relatively small compressibility and relatively high structural freedom of clinopyroxene. Extended extrapolation of elasticity data, measured at relatively low pressures, to properties at high pressures in this case may yield large errors (Zeug et al. 1993).

Another interesting question is how cations such as Fe²⁺ and Mg influence the elasticity of Ca-rich clinopyroxenes at high pressures. Although such information is highly desirable in mantle modeling as well as for understanding the structure and dynamics of the Earth’s mantle, it is not yet available, mainly for the following reasons: (1) difficulties in precise measurement of unit-cell parameters, (2) comparatively small compressibilities associated with comparatively large errors in the pressure determination (> 0.5% up to 10 GPa), and (3) complex substitution of cations in natural samples. To circumvent these problems in the present study, high-pressure single-crystal diffraction techniques were used to obtain precise unit-cell data. Synthetic end-member crystals of the bi-