The high-pressure behavior of an Al- and Fe-rich natural orthopyroxene

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ABSTRACT

A single crystal of a natural orthopyroxene with composition \( ^{36}{\text{Fe}}_{0.49}\text{Mg}_{0.16}\text{Ca}_{0.01}\text{Mn}_{0.01}\text{Mn}_{0.004} \) \( ^{36}{\text{Fe}}_{0.49}\text{Mg}_{0.76}\text{Al}_{0.084}\text{Fe}^{2+}_{0.068} \) \( ^{36}{\text{Si}}_{0.848}\text{Al}_{0.152} \) \( ^{36}\text{O}_{6} \) and space group \( \text{Pbca} \) (sample S95) was investigated at high pressure by X-ray diffraction using a diamond-anvil cell up to 9.56 GPa. No phase transitions were detected in the pressure range investigated. The unit-cell parameters, \( a, b, \) and \( c \), decrease non-linearly with pressure and show an axial compression anisotropy with a ratio \( \beta_{a}:\beta_{b}:\beta_{c} = 1.00:1.64:1.16 \). The unit-cell volume decreases non-linearly as well and with a negative variation, by about 6.3% up to 9.56 GPa. The equation of state calculated using high-accuracy volume-pressure data up to 5.5 GPa gave the following coefficients: \( V_{0} = 846.02(4) \text{Å}^3, K_{0} = 115.4(6) \text{GPa}, K' = 7.7(3) \). Among the Mg-orthopyroxenes investigated at high pressure so far S95 shows the highest bulk modulus.

Six complete intensity data were collected at 0, 0.16, 1.72, 3.95, 8.03, and 9.56 GPa. The results confirm previous conclusions regarding the compressional mechanism in orthopyroxenes. At lower pressures, compression is mostly connected to a decrease in volume of the two M-coordination octahedra, accompanied by an increased kink in the B-tetrahedral chain. At higher pressures, compression of the M sites decreases, the kink of the tetrahedral chains stops to change, and reduction in unit-cell volume is accompanied mainly by compression of tetrahedra.

This change in compressional trends results in a relatively large \( K' \) parameter and a pronounced stiffening of the structure with pressure. The presence of Al in the TB tetrahedral site influences the kink of the B tetrahedral chain, which depends on the ratio of sizes of the M2 and TB coordination polyhedra. The increased stiffness of the M polyhedra, caused by the presence of Fe, is the main reason for the high bulk modulus of S95 and its resistance to shortening of the \( c \) axis. This explains the limited shortening of the \( c \) axis in S95 and the different compressional axial anisotropy with respect to other orthopyroxenes investigated under high pressure.

Keywords: Orthopyroxene, high pressure, crystal structure, X-ray diffraction

INTRODUCTION

Several recent studies have focused on the behavior of orthopyroxene with different compositions under extreme conditions of pressure and temperature and using different experimental and computational techniques (e.g., Angel and Jackson 2002; Miyake et al. 2004; Nestola et al. 2006; Bromiley and Bromiley 2006; Cátedra and Nestola 2006; Boffa Ballaran et al. 2006; Perrillat et al. 2007; Gatta et al. 2007). The large number of investigations on orthopyroxenes is likely due to the very wide range of geological environments in which orthopyroxene is involved, from magmatic to metamorphic rocks and meteorites. In particular, orthopyroxenes are significantly abundant in the upper mantle, and most mineralogical and geophysical investigations have concentrated on shedding light on the extremely complex and geodynamic processes occurring at that depth. Knowledge of the compressional and thermal behavior of orthopyroxenes is fundamental for the understanding geological environments in which this silicate plays a crucial role.

Concerning the high-pressure behavior of orthopyroxene, X-ray diffraction studies on compressional and structural behavior have been performed on pure synthetic MgSiO3 (Hugh-Jones and Angel 1994; Angel and Hugh-Jones 1994; Angel and Jackson 2002), on pure synthetic orthoferrosilite FeSiO3 and along the MgSiO3-FeSiO3 solid solution (Hugh-Jones et al. 1997, synthetic and natural samples containing very small amounts of Al and Ca). Although the data produced in these studies concerning the bulk modulus and its first pressure derivative are consistent, the same is not true for the structural data for which several doubts remain, especially concerning the behavior of the tetrahedra and the effect of Fe, Ca, and Al admixtures at high pressure (e.g., Hugh-Jones and Angel 1994; Hugh-Jones et al. 1997; Nestola et al. 2006). More recently, Nestola et al. (2006) studied a synthetic orthopyroxene with composition \( \text{Ca}_{0.05}\text{Mg}_{0.95}\text{SiO}_{4} \) and found a different crystal structural evolution with pressure compared to previous studies. Although this investigation clarified the effect of Ca, the influence of Fe and Al, which are almost always present in natural samples, is not yet fully understood.