Pyroxmangite: A high-pressure single-crystal study

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ABSTRACT

We present the results of a single-crystal X-ray diffraction structural study on pyroxmangite in a diamond-anvil cell up to 5.6 GPa. The sample comes from Yokone-Yama, Awano Town, Tochigi Prefecture, Japan. Crystals are triclinic, centrosymmetric, with composition \[ \text{Mn}_{0.676(2)}\text{Fe}_{0.284(5)}\text{Ca}_{0.044(3)}\text{Mg}_{0.006(2)}\text{Si}_{0.001(3)}\text{O}_{6} \]. Structure refinements were performed with intensity data collected at 1.24 and 3.57 GPa on a CCD-equipped diffractometer. Lattice parameters were accurately measured with the point-detector mounted on the same instrument.

The bulk modulus of pyroxmangite fitting data to a second-order Birch-Murnaghan equation of state is \[ K_0 = 109.6(7) \text{ GPa} \]. Axial compressibility values were \[ \beta_a = 2.2(1), \beta_b = 3.3(1), \text{ and } \beta_c = 2.6(1) \times 10^{-3} \text{ GPa}^{-1} \] showing slightly anisotropic behavior, with the most compressible direction along the \( b \) axis, as commonly found in the related family of pyroxene.

Silicon tetrahedra are almost incompressible in the pressure range investigated. M polyhedra are more compressible: the volume change is smaller in the more regular octahedra M1–M4 (–3.3%) and greater in the more irregular polyhedra M5–M7 (–5.2%). Owing to the different contraction of Si tetrahedra and cation polyhedra, the sevenfold tetrahedral chains in pyroxmangite must kink to avoid misfit between chains and octahedral bands. This results in shortening of 1.2% of the \( c \) axis and a decrease in both \( O_{\parallel} - O_{\perp} \) and \( \text{Si-O-Si} \) angles.

The behavior of pyroxmangite at high \( P \) is approximately inverse to that observed at high \( T \). Compressibility data may be combined with those on thermal expansion to formulate the approximate equation of state: \[ V = V_0 \left( 1 - 9.12 \times 10^{-3} \Delta P + 3.26 \times 10^{-4} \Delta T \right) \], where \( P \) is in GPa and \( T \) in degrees Celsius.

Keywords: Pyroxmangite, pyroxenoid, equation of state, compressibility

INTRODUCTION

Pyroxmangite, nominally \( \text{MnSiO}_3 \), is a single-chain silicate belonging to the pyroxenoid polysomatic series, i.e., the series formed by a combination of layers of the two end-member structures—wollastonite (\( W, \text{Si}_2\text{O}_3 \) chains) and clinopyroxene (\( P, \text{Si}_2\text{O}_3 \) chains). Pyroxmangite has the WPP configuration, with a tetrahedral chain of seven Si-O tetrahedra, and is related to rhodonite, which represents the WP configuration, with fivefold chains of Si tetrahedra.

Pyroxmangite was first described by Ford and Bradley (1913), and its crystal structure was determined by Liebau (1959). The structure, like that of pyroxene and other pyroxenoids, may be characterized in terms of approximate closest packing of O atoms, with Si and larger cations filling tetrahedral and pseudooctahedral sites, respectively. It consists of chains of seven \( \text{Si}_2\text{O}_4 \) tetrahedra, which alternate with layers of cation-oxygen polyhedra sharing edges. Later, several refinements were carried out on various samples of natural or synthetic pyroxmangite (Ohashi and Finger 1975; Narita et al. 1977; Finger and Hazen 1978; Pinkney and Burnham 1988a) or of the isostructural pyroxferroite (Lindsley and Burnham 1970; Burnham 1971).

The mineral is triclinic, centrosymmetric, and several orientations have been chosen to describe the lattice. The choice of a \( C \)-centered cell with the chain direction parallel to the \( c \) axis and the oxygen-closest packing layer parallel to (100), although not canonical, allows better comparisons with clinopyroxene and other pyroxenoids, such as \( \beta \)-wollastonite and rhodonite.

Manganese-rich single-chain minerals are phases forming in various metamorphic assemblages (Peters et al. 1977, 1978; Brown et al. 1980; Winter et al. 1981). Pyroxmangite and rhodonite have been found in blueschist facies conditions in the Alps (Chopin 1978).

Akimoto and Syono (1972) identified four polymorphs of \( \text{MnSiO}_3 \), designated I to IV, in order of increasing pressure and having the structures of rhodonite, pyroxmangite, clinopyroxene, and garnet.

The stability of the pyroxenoids increases from rhodonite to pyroxmangite with increasing \( P \), as also demonstrated by the phase relations inferred from field data (Brown et al. 1980). Thermal expansion, compressibility, and chemical substitution effects may be significant in understanding the stability limits of these phases. The effects of temperature on pyroxmangite structure were studied by Pinkney and Burnham (1988b) who also reported a value of compressibility based on lattice parameters measured at 2 GPa. The same authors studied the structural effects of chemical substitutions in pyroxmangite and rhodonite (1988a).

In the present work, we investigate the structural behavior of pyroxmangite at high pressure, making comparisons with

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