Single-crystal X-ray diffraction of fluorapatite to 61 GPa

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ABSTRACT

Apatite is a mineral of widespread importance in Earth and planetary science. Here we examine the behavior of a natural fluorapatite (FAp) crystal from Durango (Mexico) under compression to 61 GPa. Single-crystal X-ray diffraction experiments were carried out in a diamond-anvil cell using a synchrotron source. The apatite structure persists up to 32.4 GPa. Birch-Murnaghan equation of state parameters were fit to the pressure-volume data for fluorapatite for two cases: fixing $V_0$ at its measured ambient value resulted in a bulk modulus, $K_0$, of 97.0(8) GPa and a pressure derivative of the bulk modulus, $K_0'/V_0$, of 3.3(1), while fixing $V_0$ and $K_0$ at its ambient value 90.5 GPa (derived from ultrasonically measured elastic constants) resulted in a $K_0'/V_0$ value of 4.1(1). At 35.6 GPa, fluorapatite transforms to a triclinic phase ($PT, Z=4$), designated here as fluorapatite II (FAp-II). This phase persists up to at least 61 GPa. The major structural differences between FAp and FAp-II involve the buckling of the Ca polyhedra along the c-axis and changes in the number and coordination of the Ca sites. Our study extends the pressure range over which fluorapatite has been examined by more than a factor of three, providing new insights into its structural response to high-pressure conditions.

Keywords: Apatite, high-pressure, diamond anvil cell, single-crystal X-ray diffraction

INTRODUCTION

Apatite, Ca$_5$(PO$_4$)$_3$(F,Cl,OH), occurs widely in rocky bodies in the solar system, playing an important role as a host for phosphorous and other volatiles. It is one of the most prevalent volatile-bearing phases observed in lunar samples (McCubbin et al. 2010, 2011; Boyce et al. 2014; McCubbin and Jones 2015) and is also found in meteorites (Chen et al. 1995; Sarafian et al. 2013). The apatite structure is highly adaptable and has the ability to incorporate several cations and anions, including Sr$^{2+}$, Mn$^{3+}$, Pb$^{2+}$, Br$^-$, CO$_3^{2-}$, and rare earth elements (Hughes and Rakovan 2015). Recently, there has been growing interest in the use of apatite as a diagnostic of shock metamorphism in meteorites and at impact sites (Cox et al. 2020; Kenny et al. 2020). This highlights the need for detailed characterization of the behavior of apatite minerals under static and dynamic compression.

Fluorapatite (FAp), Ca$_5$(PO$_4$)$_3$F, crystallizes in the hexagonal system (space group $P6_3/m$, $Z=2$) at ambient conditions (Fig. 1). The structure contains two types of Ca polyhedra, designated Ca1 and Ca2. The Ca1 polyhedron is a tricapped trigonal prism with ninefold coordination. The Ca1 polyhedra share (001) faces and form chains parallel to the c-axis. The cations in Ca2 are enclosed in an irregular seven-coordinated polyhedron with six oxygen bonds and one fluorine bond. PO$_4$ tetrahedra link adjacent Ca1 and Ca2 polyhedra (White and Zhi Li 2003; White et al. 2005). The F anions are located in channels running along the c-axis.

The cations in the Ca2 polyhedra define a triangle with an F anion at its center with fractional coordinates (0, 0, 1/4). Detailed descriptions of the FAp structure can be found elsewhere (White et al. 2005; Hughes and Rakovan 2015).

Experimental methods

A natural, gem-quality crystal of fluorapatite from Cerro de Mercado, Durango, Mexico (Excalibur Minerals) was used in this study. Single-crystal X-ray diffraction experiments were carried out using synchrotron-based single-crystal X-ray diffraction techniques.