Compressibility of two Na-rich clinopyroxenes: A synchrotron single-crystal X-ray diffraction study

EKATERINA A. MATROSOVA1*, LEYLA ISMAILOVA1, ANDREY V. BOBROV1,3,4, ELENA BYKOVA5, MAXIM BYKOV6, KONSTANTIN GLAZYRIN5, LUCA BINDI7,8, SERGEY V. OVSYANNIKOV6, SERGEY M. AKSENOV9,10, DMITRY YU. PUSHCHAROVSKY1, and LEONID DUBROVINSKY6

1Vernadsky Institute of Geochemistry and Analytical Chemistry of Russian Academy of Sciences, Moscow, 119991, Russia
2Koltovo Institute of Science and Technology, Skolkovo Innovation Center, 3, Moscow, 143026, Russia
3Geological Faculty, Moscow State University, Moscow, 119991, Russia
4Institute of Experimental Mineralogy of Russian Academy of Sciences, Chernogolovka, 142432, Russia
5Photon Sciences, Deutsches Elektronen-Synchrotron, Notkestrasse 85, D-22607 Hamburg, Germany
6Bayerisches Geoinstitut, University of Bayreuth, Universitätsstrasse 30, D-95440 Bayreuth, Germany
7Dipartimento di Scienze della Terra, Università di Firenze, Via La Pira 4, 50121 Florence, Italy
8FSRC “Crystallography and Photonics,” Russian Academy of Sciences, Moscow, 119334, Russia
9,10Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Moscow, 119334, Russia

ABSTRACT

Synchrotron-based high-pressure single-crystal X-ray diffraction experiments were conducted on synthetic clinopyroxenes at room temperature to a maximum pressure of 40 GPa. We studied two crystals with different compositions. A Na-Ti-pyroxene with formula (Na0.86Mg0.14)(Mg0.57Ti0.43)Si2O6 synthesized at P = 7 GPa and T = 1700 °C, and a Na-pyroxene with composition (Na0.88Mg0.08Fe0.02)(Si0.40Mg0.30Fe0.08)Si2O6 synthesized at P = 15 GPa and T = 1500 °C. These phases were found to be monoclinic with the space group C2/c and exhibit K_{20} of 106.8(2), 121.8(4) GPa, respectively. Na-Ti-pyroxene is more compressible than Fe-bearing Na-Mg-Si-pyroxene, likely due to the fact that the FeO6 octahedron is significantly more rigid than MgO6 at high pressure. The formation of Na-rich pyroxenes in the deep mantle is related to crystallization of low-degree alkaline carbonate-silicate melts formed when the crust and mantle interact during the slab descent and its stagnation in the transition zone.

Keywords: Pyroxene, single-crystal X-ray diffraction, high-pressure, high-temperature, phase transitions, equation of state, Earth’s mantle

INTRODUCTION

It is well known that pyroxenes may undergo several phase transitions with increasing P and T toward at least five different structures (Cameron and Papke 1981; Yang and Prewitt 2000). These transitions typically affect all the physical properties of the mineral including density, bulk modulus, and the orientation and dimensions of the unit-strain ellipsoid. Knowledge of the behavior of mantle materials at high P is crucial for understanding the deep Earth structure and composition. In addition, thermodynamic parameters of pyroxene end-members are critical for thermo- and geodynamic modeling of the Earth’s upper mantle (Stixrude and Lithgow-Bertelloni 2005).

The most common pyroxenes are those that contain the major elements (Ca, Mg, and Fe) in the M sites (enstatite, ferrosilite, diopside, and hedenbergite). Their early HP-XRD studies (Hazen and Finger 1977; Levien and Prewitt 1981) formed the basis for such important scientific interdisciplinary problems as comparative crystal chemistry of mantle and core minerals. The results showed that the three polyhedra (M1, M2, and Si) in pyroxene structures decrease irregularly in size and their compressibilities depend on their chemical contents. Somewhat less common are pyroxenes that incorporate larger cations, such as Na. For this reason, Na-rich pyroxenes have been much less studied.

It has long been assumed that clinopyroxenes abundant in the Earth’s crust and upper mantle contain only tetrahedrally coordinated Si. The synthesis of Na(Mg6.5Si6.5)Si2O6 pyroxene and its unit-cell parameters were originally reported based upon X-ray powder (Gasparik 1988) and single-crystal (Angel et al. 1988) diffraction. The compound was found to be monoclinic with space group P2/n. These studies have shown that clinopyroxenes may accommodate octahedrally coordinated silicon (Yang and Konzett 2005) suggesting that the stability of clinopyroxenes may be expanded to higher pressures than those previously assumed. Later Yang et al. (2009) synthesized five clinopyroxenes containing various amounts of sixfold-coordinated silicon in the Na(Mg6.5Si6.5)Si2O6–NaAlSi2O6 system at 15 GPa and 1600 °C. These authors showed that clinopyroxenes with \( ^{4} \text{Si} \leq 0.33 \) atoms per formula unit (apfu) possess C2/c symmetry, whereas those with \( ^{4} \text{Si} \geq 0.45 \) apfu crystallize with P2/n symmetry. Increasing \( ^{4} \text{Si} \) content from 0.33 to 0.45 apfu results in the formation of the discontinuity in the unit-cell parameters suggesting that the...