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Equation of state of natural apatite to 7 GPa at 300 K

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Introduction

It is generally known that apatite exists in various kind of crustal rocks, such as sedimentary, igneous and metamorphic rocks, and is one of the important reservoir of rare earth elements and large ion lithophile elements. Apatite can also include volatile elements, such as F, Cl, and OH as major constitute components. Murayama et al. [1] shown experimentally that Fluorapatite, $Ca_5(PO_4)_3F$, and Hydroxyapatite $Ca_5(PO_4)_3OH$ are stable at pressures up to 11 - 13 GPa at 1300 - 1800 K. This condition corresponds to 350 - 400 km depth in Earth's interior and their result indicates that the apatite can alive almost all conditions of the Earth's upper mantle. Apatite is, therefore, an important carrier of REE, LILE and the volatie elements to the deep mantle, and a useful tracer of the geochemical evolution of subducted crust and surrounding upper mantle. Previous study [2, 3] carried out high-pressure experiment at pressure up to 52 GPa with diamond anvil cell and measure the compressibility of apatites at ambient temperature. However, their results are less compressible relative to those by Bass [4] and reference therein. These two data sets are inconsistent. The purpose of our study is to determine the isothermal bulk modulus and its pressure derivative precisely using diamond anvil cell and to understand the compressional property of apatite.

Experimental methods

High-pressure X-ray diffraction experiments were performed using a diamond anvil cell (DAC) high-pressure apparatus. A natural apatite was used as a starting material in the experiments. The chemical composition ($Ca_5(PO_4)_3(F_{0.94}Cl_{0.06})$) was analyzed using an scanning electron microprobe (JEOL-JSM5600LV) with an energy dispersive spectrometer (Oxford) at Ibaraki University. SEM and polarization microscopic examinations showed it to be free of inclusions and chemical zoning. The diamond anvil cell has 50º open angle. A stainless steal plate was used as a gasket. The plate with 250 μm initial thickness was pre-indented to a thickness of 150 μm and about 150 μm diameter hole was electrically eroded. The apatite powder and a small amount of ruby powder were loaded into the gasket hole and were pressurized with a 4:1 methanol-ethanol mixture as a pressure transmission medium. Unit-cell parameters of apatite were measured using angler dispersive XRD at the synchrotron beam line BL13A of the Photon Factory (PF) of High Energy Accelerator Research Organization (KEK), Japan. The experimental design in situ XRD measurement at BL13A was presented by Ono et al. [5]. The incident X-ray beam was monochromatized to a wavelength of 0.4253 Å. The X-ray beam size was collimated to 30 μm in diameter. Angler dispersive XRD patterns were collected for 15 minutes with an imaging plate. The observed intensities on the imaging plate were integrated as a function of 2θ using the Fit2D in order to give one-dimensional diffraction profiles. Pressure was determined from the observed ruby fluorescence spectra.

Results

XRD data were collected to 7.12 GPa at room temperature, 300 K. Pressures were measured before and after each X-ray exposure. The estimated error (one standard deviation) was 0.22 GPa at the maximum. The X-ray diffraction data was not collected at higher pressure because the freezing of the pressure transmission medium was observed under the microscope just above 10 GPa. In this study, we did not observe a decomposition reaction of apatite to γ-$Ca_3(PO_4)_2$ + CaF_2 up to 10 GPa. The two unit-cell parameters (*a* and *c*) and volume of apatite with hexagonal system were calculated by the least-squares technique using of 24 diffraction lines. The unit-cell parameters and volume of apatite decrease smoothly with increasing pressures up to 7.12 GPa. The two unit-cell parameters show that apatite is elastically anisotropic. The volume-pressure data were fitted by the third-order Birch-Murnaghan equation of state. The results with the least-squares fit are V_0 = 524.2(3) Å^3, K_T = 92(4) GPa, and K_T' = 4.0(11) [6].

References

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