Structural refinements of magnesite at very high pressure

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ABSTRACT

Unit-cell parameters of magnesite were measured between ambient pressure and 80 GPa using angle dispersive powder X-ray diffraction. The isothermal bulk modulus determined from a third order Birch Murnaghan equation of state is K\text{r} = 108(3) GPa with K\text{r}' = 5.0(2), and V\text{r} = 279.2(2) Å³, in agreement with previously reported values. Combining this result with previous measurements, we show that magnesite with R3c structure is stable compared to the assemblage periclase + carbon dioxide at pressures and temperatures corresponding to the core-mantle boundary. Crystal structure refinements have also been carried out up to 80 GPa. The main structural change is a strong compression of the MgO₆ octahedra with increasing pressure, largely reflected in the anisotropic compression of the c axis. This compression, however, tends to level off at around 50–60 GPa. On the other hand, the CO₃ groups do not remain invariant since they undergo first a slight expansion and then a compression above the same threshold pressure of 60 GPa above which Mg-O bonds cannot compress further. Thus, in this structure-type, the energy gain due to a drastic volume reduction of the MgO₆ octahedron compensates in a given pressure range for the energy cost of the small expansion of the CO₃ carbonate unit.

INTRODUCTION

There have been a considerable number of studies suggesting that magnesite should be considered when evaluating the role of carbon in the Earth’s mantle. Magnesite (MgCO₃) is indeed a very good candidate for hosting oxidized carbon in the mantle, since experiments or calculations indicate that magnesite is, among all carbonates, the most stable at high-pressure and high-temperature (e.g., Katsura et al. 1991; Katsura and Ito 1990; Biellmann et al. 1993; Gillet 1993; Martinez et al. 1998). Numerous experiments have been dedicated to determining the compression properties (i.e., bulk modulus and its pressure derivative) of magnesite, as these govern to some extent its stability versus decomposition into a mixture of the oxides MgO and CO₂ (Redfern et al. 1993; Fiquet et al. 1994; Zhang et al. 1997; Ross 1997; Fiquet and Reynard 1999). The structural refinement of Ross (1997), however, was only carried out to 8 GPa. Here, we extend the knowledge of this crystal structure over a larger pressure domain. The high-pressure behavior of magnesite (MgCO₃) has been studied by angle dispersive X-ray diffraction up to 81 GPa. The combination of a bright focused monochromatic beam and a two dimensional detection system (imaging plates) allowed us to carry out a structural study of magnesite above 80 GPa.

EXPERIMENTAL DETAILS

Clear inclusion-free crystals from Bahia magnesite, similar to those used in Humbert and Plicque’s (1972) ultrasonic study as well as Fiquet and Reynard’s (1999) X-ray diffraction study, were chosen for this work. Samples were powdered in an agate mortar and placed in a diamond-anvil cell (Chervin et al. 1994) equipped with type Ia beveled diamonds with 100 m inner diameter culets. No pressure transmitting medium was used to avoid any chemical reaction. Magnesite crystals were intimately mixed with powdered platinum (platinum black) used as internal pressure calibrant as well as infrared absorber (Jamieson et al. 1982; Holmes et al. 1989). At each pressure increase, the sample was thoroughly annealed with a multi-mode infrared YAG (cw 280 W from Lee lasers) by focusing the laser beam into a 50 m hot spot and scanning it across the sample for several minutes. The resulting local heating in the temperature range 2000–2500 K is enough to (1) release deviatoric stresses accumulated during the compression at ambient temperature and (2) promote any possible phase transition or decomposition. This annealing is very important since it results in a dramatic release of deviatoric stress, from a value of more than 2 GPa after cold compression to about 0.5 GPa after heating at 80 GPa. This is also evidenced by a factor of two reduction of the line widths during laser heating. The diamond-anvil cell was then mounted on the dffractometer at the ESRF high-pressure beamline ID09. A focused monochromatic beam (wavelength = 0.4561 Å) was used in combination with imaging