The MnCO$_3$-II high-pressure polymorph of rhodocrosite

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**ABSTRACT**

We investigated the behavior of MnCO$_3$ in the pressure range 0–50 GPa and ambient temperature by synchrotron X-ray single-crystal diffraction technique. MnCO$_3$ maintains the calcite-type structure ($R3c$ symmetry) up to 44 GPa. Above this pressure we observed a phase transition. The high-pressure phase, MnCO$_3$-II, is triclinic, with cell parameters $a = 2.928(2)$, $b = 4.816(4)$, $c = 5.545(4)$ Å, $\alpha = 101.71(6)^\circ$, $\beta = 94.99(6)^\circ$, and $\gamma = 89.90(6)^\circ$, and $V = 76.28(10)$ Å$^3$ at 46.8 GPa. The structure is solved with the charge flipping algorithm. MnCO$_3$-II is isostructural with CaCO$_3$-VI. The density increase on phase transition is 4.4%. The occurrence of CaCO$_3$-VI structure in MnCO$_3$ composition indicates that CaCO$_3$-VI structure is also adopted by carbonates with cations smaller than calcium.

**Keywords:** Carbonates, high-pressure crystal structure, rhodocrosite, single crystal

**INTRODUCTION**

The structural behavior of carbonates at high pressure, can provide insights into the crystal chemistry of carbonates at the Earth’s mantle conditions. The evidence of structural transitions at non ambient conditions (i.e., Oganov et al. 2013) indicates that the polymorphism of carbonates is perhaps more complex than it is currently considered. Therefore, structural investigations on the various polymorphs adopted by carbonates are important studies aimed at a better understanding of the carbonate crystal chemistry in the inner Earth.

The mineral rhodocrosite, MnCO$_3$, at ambient conditions, crystallizes with the calcite-type structure, $R3c$ (Wyckoff 1920). Ono (2007) reported a phase transition at 50 GPa, after heating at 1500–2000 K. MnCO$_3$ was observed to be stable in its rhombohedral calcite-type structure up to those pressures, as confirmed by the work performed by Santillán and Williams (2004), who did not observe any transition up to 45–50 GPa. Farfan et al. (2013), reported a possible electronic transition in rhodochrosite, related to Mn behavior, in the pressure interval 25–40 GPa. They propose a possible change in symmetry. These authors also observed a change in the rhodochrosite powder pattern above 50 GPa.

To clarify some of these issues related to MnCO$_3$ behavior at nonambient conditions, we performed a single-crystal study of rhodochrosite at high pressure in the interval 0–45 GPa. The following sections we report the results based on structural refinements for each pressure step, and the structure solution achieved for MnCO$_3$-II, the high-pressure polymorph observed above 43 GPa at ambient temperature.

**MATERIALS AND METHODS**

Natural samples of rhodochrosite from Sardegna (Italy) were used for the high-pressure experiments. Microprobe analysis was performed with a JEOL Superprobe instrument (Earth Science Department, University of Milano), which indicated an almost pure MnCO$_3$ end-member, with a minor Ca content, resulting in a Mn$_{0.96}$Ca$_{0.04}$CO$_3$ formula. A prescreening single-crystal diffraction experiment performed by Oxford Diffraction instrument (Earth Science Department, University of Milano) confirmed the rhombohedral $R3c$ calcite-type structure for the sample.

The high-pressure experiments were performed with a membrane-type diamond-anvil cell at the ID09A beamline of ESRF, The European Synchrotron (Grenoble, France). The standard beamline setup was used as reported in Merlini and Hanfland (2013), with a monochromatic beam (λ = 0.41432 Å) and a spot size of approximately 30 × 30 µm$^2$ on the sample.

Two experimental runs were performed in the high- and low-pressure range, respectively. The high-pressure run was collected using a 300 µm culet diameter cell, Re gasket and Ne as pressure-transmitting medium. After one measurement at ambient condition the gas was loaded in the cell and the pressure rapidly raised to 18 GPa. Then, single-crystal data diffraction data were collected on increasing pressure every 1.5 GPa. Pressure was monitored with Ne diffraction (Fei et al. 2007) and ruby fluorescence scale (Mao et al. 1986). The difference between the two pressure sensors is negligible.

A second run in the low-pressure range (0–25 GPa) was performed, using a 600 µm culet diameter cell, stainless steel gasket, and He as pressure-transmitting medium. Single-crystal diffraction data sets were collected by 0° rotations (Busing and Levy 1967), integrating each frames on 1° step size in the angular interval -30°/+30°. As soon as a phase transition was detected above 43 GPa, reciprocal space sampling was increased by collecting data at different χ axis positions, to access all the available reciprocal space allowed by the diamond-anvil cell opening cone.

Raw single-crystal data were handled by the Crysalis software (Oxford Diffraction 2008), extracting lattice parameters and intensity data. Crystal-structure analysis was performed with the Jana2006 software (Petricek et al. 2014). Structure solution was achieved with the Superflip (Palatinus and Chapuis 2007) program and successive Fourier difference analysis.

**RESULTS**

**High-pressure behavior of R3c MnCO$_3$**

The crystal structure of MnCO$_3$ at ambient conditions is in agreement with literature data (Graf 1961; Maslen et al. 1995). It is calcite-type, $R3c$, where layers of Mn cations alternate with parallel (CO$_3$)$^2$ groups. Mn features an octahedral coordination. The geometry of the MnO$_6$ octahedra results in six equal...