Compression behavior of rhodochrosite, $MnCO_3$

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The structure of rhodochrosite, $MnCO_3$, is similar to that of calcite, $CaCO_3$. The carbonate ion is a planar geometry and layers of CO_3 groups lie normal to the *c* axis of its structure. The Mn^{2+} cations and their six coordinating oxygen ions form octahedra. The octahedrally coordinated Mn^{2+} cations have the five *d* electrons and should be high-spin state at an ambient pressure, judging from the Mn-O distance. The ionic radius of a transition metal cation in the low-spin state is typically about 10 % smaller than that of the cation in its high-spin state. Therefore, under sufficiently high pressures, octahedrally coordinated Mn^{2+} cations are expected to undergo a high-spin to low-spin transition, because the crystal field splitting energy increases with decreasing Mn-O distance under high pressure. We expect that such transition can be observed by in-situ high resolution X-ray diffraction experiments under high pressure.

Pressure was generated by a lever-and-spring type diamond anvil cells (DAC) with 450 μm culet diamond anvils. Fine powder samples of rhodochrosite, $MnCO_3$, were loaded with a small ruby chip in the 150 μm diameter hole of a preindented inconel 750X gasket and a mixture of methanol : ethanol = 4 : 1 was used as the pressure medium. Pressures were measured by the usual ruby fluorescence method before and after each exposure.

Diffraction patterns were obtained up to about 30 GPa using a synchrotron X-ray in combination with an imaging plate on BL10XU, which was specially constructed beamline for DAC experiments. The X-ray was monochromatized to the wavelength of 0.41897 Å and was collimated to 50 μm in diameter. The distance between sample and the detector was 300.00 mm. The exposure time for each run was one hour.

No obvious change could not be observed in the X-ray diffraction patterns. However, the values of c/c_0 suggest that some change occurs above 23 GPa. The axial compressions a/a_0 and c/c_0 are plotted as a function of pressure in Fig. 1. The *c* axis is about two times more compressible than the *a* axis up to 23 GPa. The volume-pressure data is shown in Fig. 2 and indicates that some change occurs obviously above 23 GPa. Thus we propose a separate equation of state up to 23 GPa only and the isothermal bulk modulus are determined from the Birch-Murnaghan equation of state. If the pressure derivative of the bulk modulus, K'_0, is assumed to be 4, then the calculated bulk modulus is 129(3) GPa. This value is significantly larger than that of 95(9) GPa reported in Martens et al.(1982). It remains unclear whether the change observed in this experiments suggests a high-spin to low-spin transition, and further high pressure experiments are needed to resolve this problem.

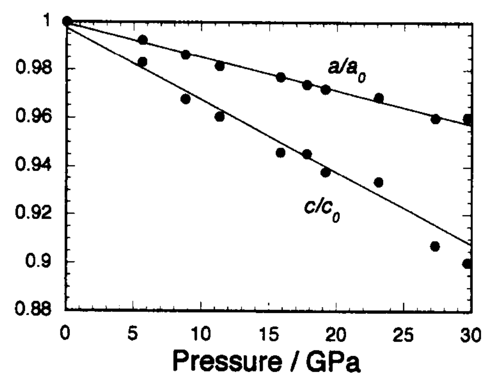

Fig. 1. Axial compressions a/a_0 and c/c_0 as a function of pressure. Lines represent linear fits up to 23 GPa

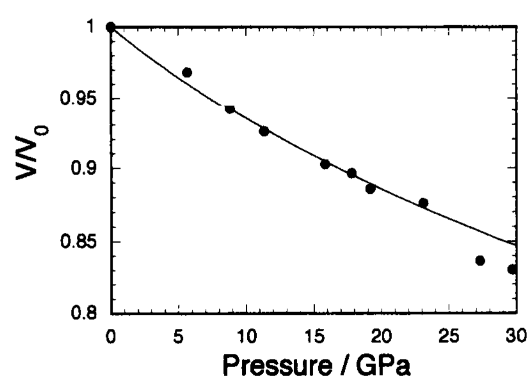

Fig. 2. Compression curve of $MnCO_3$. The line represents the equation of state best fit up to 23 GPa.

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