

New high phase of manganese carbonate

Shigeaki ONO*¹

¹ Institute for Research on Earth Evolution (IFREE), Japan Agency for Marine-Earth Science and Technology (JAMSTEC), Yokosuka, Kanagawa 237-0061, Japan

Introduction

Recently, the study of the alkaline-earth carbonates at high pressures and high temperatures has been a subject of great interest, because several new high-pressure phases of alkaline-earth carbonates were discovered by both experiments and theoretical simulations. Although Mg and Ca carbonates are likely to be the most abundant carbonate minerals in the Earth, the behaviour of these carbonates under extreme high-pressure conditions is still unclear. The phase behaviour of MnCO_3 has attracted much less attention than Mg and Ca carbonates in the past. It is known that the structure of the larger-cation compounds is often used as a structure model for the smaller-cation compounds. The ionic radius of Mn is intermediate between Mg and Ca. On the basis of this criterion, MnCO_3 is a good analogue for understanding the difference in high-pressure phase behaviour between Mg and Ca carbonates. At ambient pressures, MnCO_3 rhodochrosite is rhombohedral (space group $R\bar{3}c$), isotopic with magnesite (MgCO_3) and calcite (CaCO_3). Therefore, MnCO_3 is likely to be a key to understand the transition sequence of alkaline-earth carbonates.

Experimental

High-pressure X-ray diffraction experiments were performed using LHDAC high-pressure apparatus [1]. A motor-driven diamond cell with a 60° conical aperture was used [2]. The starting material of rhodochrosite (purity 99.98%) had the rhombohedral structure, space group $R\bar{3}c$, which was identified by the X-ray powder diffraction. Platinum powder was mixed with the sample to absorb the laser radiation and so provide a heat source. It was also used as an internal pressure calibrant. The sample was initially compressed at room temperature. After being kept at the temperature and press load for a given time, the samples were quenched by shutting off the laser. The typical heating time was 5-10 min at each P-T condition. The heated samples were probed using angle-dispersive X-ray diffraction at the synchrotron beam line BL13A, Photon Factory. A monochromatic incident X-ray beam was collimated to a diameter of 20-30 μm , and the angle-dispersive X-ray diffraction patterns were obtained on an imaging plate (Rigaku, Japan).

Results and Discussion

The pressure was directly increased to 54 GPa at room temperature. After compression, the sample was heated at 1500~2000 K. The pressure was likely to increase several GPa during heating, because of the influence of the

thermal expansion of the sample. After heating, the diffraction pattern of the sample changed drastically (Fig. 1). In addition to peaks arising from the platinum, many new peaks were observed. This indicates that rhodochrosite had transformed into a new high-pressure phase. Although a couple of unexpected small spot peaks were observed in the X-ray diffraction data, these peaks seemed to be unrelated with the sample. The diffraction rings from the sample were continuous on the imaging plate. In contrast, unexpected extra small peaks were observed as spots on the imaging plate. This indicated that the spot peaks were not from the powder diffraction pattern of the sample. After the synthesis of the new phase, the pressure was decreased to 34 GPa and the sample was heated again. Most peaks of the new high-pressure phase disappeared, and major peaks appeared after heating belonged to rhodochrosite. The diffraction pattern of the sample showed that the back transformation from the new phase to rhodochrosite had occurred. The experimental results indicate a transition pressure of ~50 GPa. The diffraction pattern of the new high-pressure phase can be indexed with an orthorhombic unit-cell with $a = 5.361 \text{ \AA}$, $b = 8.591 \text{ \AA}$ and $c = 9.743 \text{ \AA}$, with a unit cell volume of 448.8 \AA^3 at 54.1 GPa and 300 K, with 12 molecules per unit cell ($Z = 12$) [3].

References

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- * sono@jamstec.go.jp

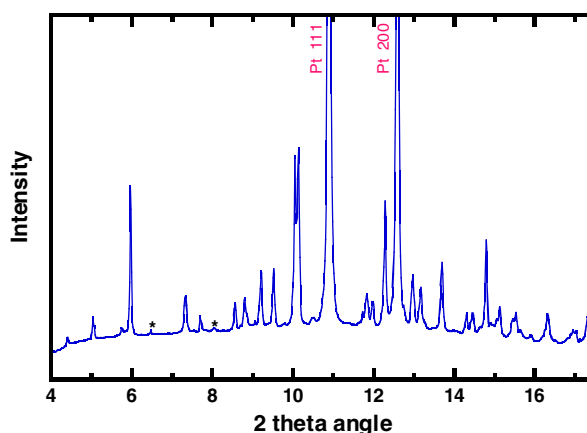


Figure 1. Observed X-ray diffraction pattern of MnCO_3 phase at 54 GPa and 300 K.