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Pressure-induced phase transition of $BaCO_3$

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Introduction

It is known that barium carbonate ($BaCO_3$) is a good analogue for investigating the stability and structure of $MgCO_3$ and $CaCO_3$. Witherite is the stable phase of $BaCO_3$ under ambient conditions. The structure of witherite, with space group *Pmcn*, is same as that of aragonite, which is a high-pressure phase of $CaCO_3$. However, a significant discrepancy in the crystal structures of the high-pressure phases of $BaCO_3$ has been reported in previous high-pressure studies. In the case of carbonate studies at high pressures, a kinetic effect on the phase transformation sometimes misleads the experimental interpretations [1]. Furthermore, some high-pressure minerals cannot be quenched to ambient conditions. Therefore, it is necessary to carry out the heating of a sample to induce the observed phase transformation in *in situ* high-pressure diffraction studies to identify the stable high-pressure phases.

Experimental

High-pressure X-ray diffraction experiments were performed using a laser-heated diamond anvil cell high-pressure apparatus. Synthetic powdered $BaCO_3$, (purity = 99.99%), witherite with an aragonite-type structure, *Pmcn*, which is the stable phase under ambient conditions, was used as the starting material. Platinum (Pt) powder was mixed with the sample to absorb the laser radiation to provide a heat source, and it was also used as an internal pressure calibrant. The samples were heated with a laser to overcome any potential kinetic effects on possible phase transitions. The samples were probed using an angle-dispersive X-ray diffraction technique at the synchrotron beam lines BL13A, Photon Factory in Japan [2]. A monochromatic incident X-ray beam was used. The X-ray beams were collimated to a diameter of 15-30 μm, and the angle-dispersive X-ray diffraction patterns were obtained on an imaging plate.

Results and Discussion

In the first experimental run, the sample was compressed to 16 GPa. Before laser heating was carried out, the diffraction pattern of the sample showed broad peaks, reflecting the presence of a compression-related differential stress. The sample was then heated 10 minutes to ~1300 K to relax the differential stress and to synthesize the high-pressure $BaCO_3$ phase. During the heating stage, new diffraction peaks appeared, and these remained stable after the temperature quench. The observed diffraction pattern after heating is shown in Fig. 1. The new peaks could not be indexed using any of the known high-pressure phases of $BaCO_3$. This indicates that the new high-pressure phase could be synthesized at 16 GPa at high temperatures. Following decompression, the new phase was not recovered. The recovered sample transformed into the known orthorhombic structure. Thus, this new phase could not be quenched to ambient conditions. The diffraction peaks of the new phase were reasonably indexed to an orthorhombic symmetry, and there are two molecules of this phase in a unit cell (Z = 2). The lattice parameters at 16.2 GPa and 300 K, for example, are: a = 4.803 Å, b = 5.306 Å, and c = 4.459 Å, with a unit cell volume of 113.66 $Å^3$ for the orthorhombic cell [3]. The most reasonable space group of this phase is *Pmmn*. The C^{4+} cations exhibit a three-fold coordination with the oxygen ions. Twelve-coordinate Ba^{2+} cations occur in the new structure. We confirmed that this new phase is stable up to at least 70 GPa.

References

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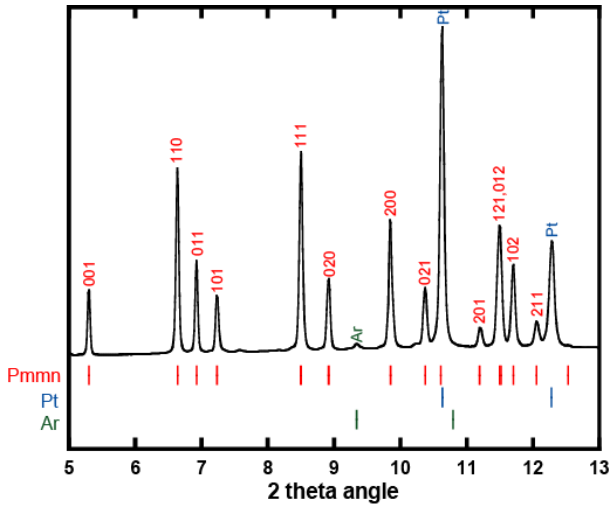

Figure 1. Diffraction pattern of the new $BaCO_3$ phase. This diffraction pattern was obtained at 16 GPa. Numbers for peaks represent *hkl*'s of orthorhombic symmetry (space group *Pmmn*). Pt and Ar represent peaks of platinum and argon, respectively. The wavelength of the monochromatic incident X-ray beam was 0.4125 Å.