

## Stability and equation of state for aragonite-structure carbonates

QIONG LIU<sup>1,2</sup>, MEILI WANG<sup>1,2</sup>, SHUFANG NIE<sup>1,2</sup>, YE WU<sup>1,2</sup>,  
 YANG LIU<sup>2</sup>, JING GAO<sup>1,2</sup>, XIAOZHUO WEI<sup>2</sup>,  
 BAOSHENG LI<sup>2,3</sup>, XIANG WU<sup>1,2</sup> AND HEJIN WANG<sup>1,2</sup>

<sup>1</sup>Key Laboratory of Orogenic Belts and Crustal Evolution, MOE, Peking University, Beijing 100871, China

<sup>2</sup>School of Earth and Space Sciences, Peking University, Beijing 100871, China

<sup>3</sup>Mineral Physics Institute, State University of New York, Stony Brook, New York 11794, USA

The phase evolution and thermal expansivity of synthesized orthorhombic  $\alpha$ -BaCO<sub>3</sub> and  $\alpha$ -SrCO<sub>3</sub> were studied up to 1413 K using high-temperature powder X-ray diffraction. In addition, the phase transitions and compressibilities for these two carbonates were examined by synchrotron X-ray diffraction combined with diamond-anvil cells up to 30 GPa and 15 GPa at room temperature, respectively. SrCO<sub>3</sub> and BaCO<sub>3</sub> transform from orthorhombic phase (Pmcn) to trigonal phase (R-3m or R3m) and further to cubic phase (Fm-3m) at a higher temperature (Boeke, 1913; Lander, 1949; Baker, 1962; Stromme, 1975). SrCO<sub>3</sub> (Pmcn to P21212) and BaCO<sub>3</sub> (Pmcn to Pmmn) also undergo phase transformation with increasing pressure (Ono et al. 2005; Townsend et al. 2013, and references therein). The phase transition temperatures and pressures are obtained for both carbonates. Both carbonates in aragonite structure display anisotropy in thermal expansivity and compressibility, with the *c*-axis much more expansible and compressible than the *a*- and *b*-axis, which can be explained by their structure, where the weak ionic bond M–O (Ba–O, Sr–O) controls the *c*-axis, while the strong covalent bond C–O in the plane of CO<sub>3</sub> groups and the basal component of the ionic bond M–O dominate the *a*- and *b*-axis. For the high temperature trigonal phase of  $\beta$ -BaCO<sub>3</sub>, the thermal expansion along the *a*-axis is negative, and the thermal expansion along the *c*-axis is 2.7 times the contraction along the *a*-axis, which resulting in a positive volume expansion. Thermal expansion coefficient of the cubic high-temperature phase  $\gamma$ -BaCO<sub>3</sub> is derived for the first time. By combining with previous studies on aragonite (CaCO<sub>3</sub>), this study reveals a contrasting behavior of the thermal expansion and compression for aragonite-group carbonates (CaCO<sub>3</sub>, SrCO<sub>3</sub>, and BaCO<sub>3</sub>) as a function of cation size (i.e. constant volume thermal expansion vs. increasing compressibility with an increase in cation radius) which agrees with the empirical formula proposed by Hazen et al.(2000).