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Effect of cationic substitution on the pressure-induced phase transitions in calcium carbonate

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Abstract

The high-pressure $CaCO_3$ phase diagram has been the most extensively studied within the carbonates group. However, both the diverse mineralogy of carbonates and the abundance of solid solutions in natural samples require the investigation of multi-component systems at high pressures (*P*) and temperatures (*T*). Here we studied a member of the $CaCO_3$–$SrCO_3$ solid-solution series and revealed the effect of cationic substitution on the pressure-induced phase transitions in calcium carbonate.

A synthetic solid solution $Ca_{0.82}Sr_{0.18}CO_3$ was studied in situ by Raman spectroscopy in a diamond-anvil cell (DAC) up to 55 GPa and 800 K. The results of this work show significant differences in the high-pressure structural and vibrational behavior of the $(Ca,Sr)CO_3$ solid solution compared to that of pure $CaCO_3$. The monoclinic $CaCO_3$-II-type structure (Sr-calcite-II) was observed already at ambient conditions instead of the "expected" rhombohedral calcite. The stress-induced phase transition to a new high-pressure modification, termed here as Sr-calcite-IIIc, was detected at 7 GPa. Sr-calcite-VII formed already at 16 GPa and room *T*, which is 14 GPa lower compared to $CaCO_3$-VII. Finally, crystallization of Sr-aragonite was detected at 540 K and 9 GPa, at 200 K lower *T* than pure aragonite. Our results indicate that substitution of Ca^{2+} by bigger cations, such as Sr^{2+}, in $CaCO_3$ structures can stabilize phases with larger cation coordination sites (e.g., aragonite, $CaCO_3$-VII, and post-aragonite) at lower *P-T* conditions compared to pure $CaCO_3$. The present study shows that the role of cationic composition in the phase behavior of carbonates at high pressures should be carefully considered when modeling the deep carbon cycle and mantle processes involving carbonates, such as metasomatism, deep mantle melting, and diamond formation.

Keywords: Deep carbon cycle, calcium carbonate, solid solution, phase diagram, phase transition, high pressure, vibrational spectroscopy