

## MS18-O5 Structural trend of alkaline carbonates under high pressure

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The high-pressure behavior of alkaline carbonates is of practical interest due to the catalytic activity of these compounds in the process of diamond's crystals growth. The fundamental interest is in the construction of the high-pressure structural trend and its comparison with such trends of other  $A_xCO_3$  carbonates and  $A_xB$  binary compounds. We determine this trend based on complex experimental and theoretical investigation of high-pressure behavior of  $Li_2CO_3$ ,  $Na_2CO_3$  and  $K_2CO_3$ . Theoretical investigation is based on the evolutionary crystal structure prediction algorithms (USPEX package) and density functional theory (VASP package), pressure range 0-100 GPa. Experiments were performed in the large-volume multi-anvil apparatus installed at the BL04B1 beamline of the Spring-8 synchrotron radiation facility, pressure range 2-30 GPa.

The sequence of theoretically revealed transitions is presented in Fig. 1. All cation arrays of the high-pressure structures are of  $AIB_2$ -type, ideal or deformed. The simplest high pressure behavior is observed for  $Li_2CO_3$ , which directly transforms to ideal (hexagonal)  $AIB_2$ -type at 8 GPa and stable in this form up to 100 GPa.  $Na_2CO_3$  transforms to ideal  $AIB_2$ -type at 5 GPa and then to deformed monoclinic (P2/m)  $AIB_2$ -type at 35 GPa.  $K_2CO_3$  does not adopt ideal  $AIB_2$ -type and at 12 GPa transforms to triclinic (P-1), and then to monoclinic phase (C2/c) at 53.5 GPa. The last one is the analogue of P2/m-phase of  $Na_2CO_3$ . The presented results are in good agreement with results of our experiments, according to which ambient  $\gamma$ - $Na_2CO_3$  transforms to ideal  $AIB_2$ -structure at 12 GPa, and  $\gamma$ - $K_2CO_3$  transforms to a new phase at 12 GPa. The transformation of  $\gamma$ - $Li_2CO_3$  into ideal  $AIB_2$ -structure was observed in the experiments of Grzechnik and co-authors [Grzechnik *et al.*, 2003] above 10 GPa.

Thus, according to our results cation arrays of alkaline carbonates transforms from anti-CaF<sub>2</sub> ( $Li_2CO_3$ ) and from Ni<sub>2</sub>In ( $Na_2CO_3$ ,  $K_2CO_3$ ) types to  $AIB_2$ -type. This trend is consistent with that of alkaline sulfides (selenides, tellurides), which under compression goes through the series of phase transitions: anti-CaF<sub>2</sub>---PbCl<sub>2</sub>---Ni<sub>2</sub>In--- $AIB_2$ . The correspondence of these two trends is supported by the fact that PbCl<sub>2</sub>-type structure was revealed in our calculations as the possible phase of  $Na_2CO_3$  stable under ambient conditions.

**References** Grzechnik, A., P. Bouvier, and L. Farina (2003), High-pressure structure of  $Li_2CO_3$ , *J. Solid State Chem.*, 173(1), 13-19.

$Li_2CO_3$ :  $\gamma$ - $Li_2CO_3$  (anti-CaF<sub>2</sub>)  $\xrightarrow{8\text{ GPa}}$  P6<sub>3</sub>/mcm ( $AIB_2$ )  
 $Na_2CO_3$ :  $\gamma$ - $Na_2CO_3$  (Ni<sub>2</sub>In)  $\xrightarrow{5\text{ GPa}}$  P6<sub>3</sub>/mcm ( $AIB_2$ )  $\xrightarrow{35\text{ GPa}}$  P2/m ( $AIB_2$ -deformed)  
 $K_2CO_3$ :  $\gamma$ - $K_2CO_3$  (Ni<sub>2</sub>In)  $\xrightarrow{12\text{ GPa}}$  P1 ( $AIB_2$ -deformed)  $\xrightarrow{53.5\text{ GPa}}$  C2/c ( $AIB_2$ -deformed)

Figure 1. High-pressure phase transitions of  $Li_2CO_3$ ,  $Na_2CO_3$ , and  $K_2CO_3$ .

**Keywords:** pressure, crystal structure prediction, DFT, experiment, synchrotron radiation