The high-pressure behavior of alkaline carbonates is of practical interest due to the catalytic activity of this 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 A₂CO₃ carbonates and A₂B binary compounds. We determine this trend based on complex experimental and theoretical investigation of high-pressure behavior of Li₂CO₃, Na₂CO₃ and K₂CO₃. 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 AlB₂-type, ideal or deformed. The simplest high pressure behavior is observed for Li₂CO₃, which directly transforms to ideal (hexagonal) AlB₂-type at 8 GPa and stable in this form up to 100 GPa. Na₂CO₃ transforms to ideal AlB₂-type at 5 GPa and then to deformed monoclinic (P2/m) AlB₂-type at 35 GPa. K₂CO₃ does not adopt ideal AlB₂-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 Na₂CO₃. The presented results are in good agreement with results of our experiments, according to which ambient γ-Na₂CO₃ transforms to ideal AlB₂-structure at 12 GPa, and γ-K₂CO₃ transforms to a new phase at 12 GPa. The transformation of γ-Li₂CO₃ into ideal AlB₂-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-CaF₂ (Li₂CO₃) and from Ni₃In (Na₂CO₃, K₂CO₃) types to AlB₂-type. This trend is consistent with that of alkaline sulfides (selenides, tellurides), which under compression goes through the series of phase transitions: anti-CaF₂ --- PbCl₂ --- Ni₃In --- AlB₂. The correspondence of these two trends is supported by the fact that PbCl₂-type structure was revealed in our calculations as the possible phase of Na₂CO₃ stable under ambient conditions.

References

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