Poster

Crystallography of the pressure-induced structural phase transitions in $K_2Ca(CO_3)_2$ and $K_2Ca_2(CO_3)_3$ carbonates

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Presence of K-rich carbonatitic melts in upper mantle and discovery of dense K-Ca carbonates as mineral inclusions in diamonds [1] demonstrated the rising importance of understanding the role of potassium within our planetary deep carbon cycle. Within the K_2CO_3-$CaCO_3$ system [2], there are two selected phases, i.e. $K_2Ca(CO_3)_2$ and $K_2Ca_2(CO_3)_3$ of which structural polymorphism was investigated under in-situ high-pressure conditions.

$K_2Ca(CO_3)_2$ phase, also known as the low-T form of the mineral *buetschliite,* is described as trigonal structure (space group *R-3m*). [3]. The in-situ HP Raman spectroscopic investigations reveal a transition at ~6.2 GPa [4], which has recently been confirmed [5]. Spectra for both compression and decompression show a distinct splitting of several bands, whereas it is also observed that even several new bands arise. With additional HPHT Raman investigations, up to 300°C, bands that previously split at ~6.2 GPa at RT, exhibit this behaviour at 8 GPa. Further on, HP sXRD analysis reveals that initial symmetry of *R-3m* is maintained up to ~6.5 GPa, while the data collected at 6.85 GPa could be indexed both with trigonal and monoclinic unit cell. Overall, refinement of *C2/m* structure model shows better agreement factors. Therefore, detailed measurements in range 5-10 GPa concluded proposed reversable phase transition *R-3m* - *C2/m*. This transformation is followed up by a change in the coordination of K atoms, as it progresses from 9-fold in *R-3m*, to 12-fold coordination in *C2/m* space group. Observable volume changes are rather small, although, most importantly, discontinuous in character, which is indicative of the first order transition.

$K_2Ca_2(CO_3)_3$ phase has been reported earlier [6] in an acentric trigonal structure corresponding to a *R3* model, but showing conspicuous ADP's and bond lengths. The in-situ HP Raman spectroscopic investigations of a synthetic sample reveal a pressure-induced transition at ~2.6-4.2 GPa, with the spectrum of LP-phase exhibiting rather broad bands sharpening up to distinct modes observable for the HP phase. Compression and decompression exhibit a remarkable hysteresis for the critical transition. The transformation is also obvious from lattice changes, related to a pronounced change in the *c/a* ratio of the trigonal metrics, without being accompanied by significant volume changes and while maintaining the apparent *R*3 space-group symmetry. Structural crystallography of the HP-phase revealed a proper well-ordered model in *R*3 symmetry with significant changes of the orientation of the CO_3 group. The crystallographic re-investigation of the LP-phase confirm the originally proposed trigonal lattice, and sXRD data provide no evidence for any superstructure, violation of the *R*-centering, or any lower symmetry. Refinements show that disorder according to split positions, in particular for K2 and the oxygen sites, provide a more reasonable local stereochemistry. Therefore, a disordered *R*3 model is proposed for the LP structure, with increasing pressure gradually reducing the magnitude of disorder on approaching the critical transition pressure while maintaining the same trigonal symmetry, whereas it reaches a fully ordered state beyond the transition point. The observed transition appears thus to be isosymmetric, transforming from a disorder *R*3 to a properly ordered *R*3 arrangement.

[1] Logvinova, A. M., Shatskiy, A., Wirth, R., Tomilenko, A. A., Ugap'eva, S. S., Sobolev, N. V. (2019). *Lithos*, 342-343, 463-467.

[2] Arefiev A.V., Shatskiy A., Podborodnikov I.V., Rashchenko S.V., Chanyshev A.D., Litasov K.D. (2019). *Phys. Chem. Miner*., 46, 229–244.

[3] Pabst A (1974). *Am. Mineral*., 59:6.

[4] Likhacheva A.Yu., Milos S., Romanenko A.V., Goryainov S.V., Semerikova A.I., Rashchenko S.V., Miletich R., Shatsky A. (2023). *J. Raman Spectr*., 1.

[5] Zeff, G., Kalkan, B., Armstrong, K. et al. (2024). *Phys. Chem. Minerals* 51, 2.

[6] Winbo, C., Boström D., Göbbels M., (1997). *Acta Chem. Scand*., 51, 387-391.