Poster

Disordered rhombohedral $K_2Ca_2(CO_3)_3$: a supposedly transient state within an ambiguous transformation route on decompression

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Within the K_2CO_3-$CaCO_3$ system on *P,T* variation relevant to the Earth's geotherm [1], trigonal $K_2Ca_2(CO_3)_3$ is one of the known solid key phases with an apparent stability under the conditions of formation. Early descriptions report on intensive polysynthetic twinning in morphologically trigonal crystals [2], and the structure was later solved according to acentric *R3* space-group symmetry, but with a model proposed by Winbo et al. (1997) [3] showing conspicuous ADP's and bond lengths.

High-pressure Raman spectroscopy on isothermal compression and decompression clearly indicate a phase transition, that exhibits pronounced hysteresis with a transition at ~4.2 GPa under compression, and a re-transformation latest at ~2.6 GPa on pressure release. Apart from the evidence of the thermodynamic character being first order, the significant spectral changes associated with the phase transformation are remarkable: While the Raman spectra of the low-pressure (LP) phase are characterized by comparatively broad and sometimes strongly overlapping peaks, the spectral modes observed for the high-pressure (HP) phase are relatively sharp and show significantly smaller half-widths. These changes, that mark the actual transition point, are reversible and follow the observed hysteresis within the pressure interval between 2.6 and 4.2 GPa.

Crystallographic investigations were carried out by means of single-crystal diffraction, both at ambient conditions and at hydrostatic high pressures in a diamond-anvil cell. Various synchrotron data sets from beamtimes at DESY, ESRF, and Elettra were recorded on synthetic samples of different age, all of them obtained from equivalent high-pressure syntheses in a multi-anvil press. It was rather unexpected that the structure of the HP-phase was comparatively easy to solve and immediately gave satisfactory refinements in the same space-group symmetry *R3*. Compared to original LP-structure model reported by [3], the most significant difference of the HP-structure was found for the orientation of CO_3 group, which are significantly less inclined off the (0001) plane direction, which in turn yields a significant discontinuity in the evolution of the *c/a* ratio across the transition point.

On the contrary, the LP-phase turned out to be partially ambiguous and sometimes produced different results for the different data sets. One of the most notable discrepancies were different volumes for different unit cells, on the one hand metrically perfect trigonal lattices (V = ~1276.0 Å^3), but also triclinic unit cells of pseudo-trigonal metrics with a smaller volume (V = ~1269.8 Å^3). It can be assumed that these differences correlate with different ages of the sample since the time of synthesis. Using a fresh sample, a stable refinement in *R3* was achieved for a metrically perfect trigonal lattice according to the original Winbo *R3* model [3]. The sXRD data provided no evidence for any superstructure, violation of the *R*-centering, or lowering the space-group symmetry. However, only the refinement of a disordered structural model provides a more reasonable local stereochemistry. K2 and Ca2 occupy in this new model each split positions, as well as all oxygen atoms compared to the apparently ordered Winbo model, which obviously represents the average structure of here reported disordered *R3* structure. Nevertheless, the differences between the two *R3* lattices are obvious, as they display completely different *c/a* ratios, as a consequence of the change in the orientation of the carbonate groups.

Here we present the findings of the structure investigations, which includes the revised disordered *R3* structure model for the LP-phase as found for a fresh sample. The disorder appears to originate from the carbonate groups, as exemplified in other carbonate phases,
e.g. [4], with a characteristic non-uniform distribution of CO_3 group across the whole structure in a transient state. New proposed model reveals additional structural information, related to defining both, initial and intermediate stability states and a transformation route on decompression, which might include a stable triclinically distorted phase.

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