MS20. High pressure solid state chemistry

Chairs: Natalia Dubrovinskaia, Wilson Crichton

MS20-P1 Dynamic compression and time-resolved XRD across the phase boundaries of the high-P polymorphs of $CaCO_3$

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Calcium carbonate, $CaCO_3$, shows a rich polymorphism with in total 7 phases at ambient and non-ambient pressure and temperature conditions. Compression of calcite, the trigonal low-P form (space group R-3c), results in the transformation to a monoclinic structure ("calcite-II", space group P21/c) at P> 1.4 GPa and hereafter into two triclinic structures (phases III and IIIb, space group P-1) [1-3]. Phase IIIb is considered to be either metastable or have a stability field at high-P low-T conditions [3]. One of the speculations about the existence of the phases III and IIIb was the fact that compression rates appear to determine the structural stability [1]. Therefore, a time-resolved XRD in-situ study under controlled compression rates using a dynamic diamond-anvil cell (dDAC) was accomplished at SSRL (Standford Synchrotron Radiation Lightsource) BL 10-2 beamline on a polycrystalline CaCO3 sample compressed under rates of 0.0052 to 0.017 GPa/frame for 1 second exposure time per frame using a Dectris Pilatus 300k detector. The I-II transition was found to reveal a smooth shift of the XRD Bragg peaks corresponding to the splitting, which follows the trigonal-to-monoclinic distortion within a pressure interval between 1.57 and 1.77 GPa. The transition from II to III starting at 2.67 GPa is characterized by the coexistence of III and IIIb, while at 2.98 GPa the XRD pattern only consists of the lines of phase III. The field of III+IIIb coexistence slights varies with the compression rate (2.67-2.98 GPa at 0.0052 GPa/sec; 2.89-3.04 GPa at 0.017 GPa/sec), and corresponds to the pressure range for IIIb as recently reported [3]. Nevertheless, the XRD patterns recorded with the dDAC reveal a further change at P > 4.68 GPa, which has not been yet identified but might be considered as a new phase. The results of this dynamic compression are also compared to the findings of the Raman investigations under non-hydrostatic conditions, which have been carried out in order to identify the influence of stress on shifting phase boundaries.

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