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9

Local contact(s): Philip Pattison*Received at ESRF:***Names and affiliations of applicants** (* indicates experimentalists):

Alexandra Friedrich, Laboratory of Crystallography, ETH Zürich, CH-8092 Zürich

Martin Kunz, Laboratory of Crystallography, ETH Zürich, CH-8092 Zürich

Ronald Miletich, Laboratory of Crystallography, ETH Zürich, CH-8092 Zürich

Report:

As a part of a project with the aim to study the pressure dependency of hydrogen-bonded systems and their structural changes with pressure, we investigated Sr(OH)₂ and the two polymorphs (β and α phases) of Ba(OH)₂. Our investigations were carried out by means of high-pressure X-ray powder diffraction and focussed on pressure-induced phase transitions. The CO₂- and H₂O-sensitive powder samples were loaded cryogenically in an ETH diamond-anvil cell with argon as pressure-transmitting medium. Due to the fast MAR345 image plate system, we were able to carry out 6 individual cell loadings and to measure about 40 pressure points at two different detector distances each (170 mm and 380 mm at $\lambda=0.8$ Å). A long distance served for an improvement of resolution as needed for unit-cell determinations and a short one for maximization of the structural information approachable up to $45^\circ 2\theta$. The pressure was increased in steps of 1-2 GPa up to 13 GPa. Especially the Ba(OH)₂ system shows a very complex behavior. Already at ambient conditions there are two polymorphs known. β -Ba(OH)₂ [$P2_1/n$, $a=9.4095(1)$ Å, $b=7.95154(8)$ Å,

$c=6.77451(7)\text{\AA}$, $\beta=95.8124(7)^\circ$] is the stable phase at low T, while the α -phase [$Pnma$, $a=11.0113(3)\text{\AA}$, $b=16.4994(4)\text{\AA}$, $c=7.0952(2)\text{\AA}$] is stable at high T above 525 K [1] and can be metastably recovered to room T. At least two phase transitions were detected in β -Ba(OH)₂, each indicated by the appearance of additional low-angle peaks. The low-P β_2 -phase could be explained by a doubling of the unit cell volume [$P2_1/c$, $a\sim 11.531\text{\AA}$, $b\sim 7.742\text{\AA}$, $c\sim 10.765\text{\AA}$, $\beta\sim 108.5^\circ$]. Between 8 and 9 GPa the β_3 -phase is formed, which possibly might be indexed by a cell four times larger than the ambient-pressure β -phase, with doubled a and c axes compared to the β_2 -phase [$P2_1/m$, $a\sim 22.06\text{\AA}$, $b\sim 6.97\text{\AA}$, $c\sim 19.71\text{\AA}$, $\beta\sim 111.9^\circ$]. This β_3 -phase may show another phase transition (β_4) between 9.2 and 10 GPa. Studying the α -phase also shows a low-P phase transition towards an α_2 -phase, and a second one between 7.7 and 9 GPa (α_3 -phase). On pressure release down to 0.3 GPa, the α_3 -phase does not revert to the high-T α -phase, but transforms to the β_2 -phase. The evaluation of our data is still ongoing. These results will be highly complimentary to our previous T-dependent neutron-diffraction studies of the Ba(OH)₂ system at the ILL, where we discovered a new low-T α_m -phase [2]. This enables us to compare the low-T with the high-P α -phases.

We also calculate equations of state, and first compressibility data are available from first refinement results for β -Ba(OH)₂ [$V_0=501.968(9)\text{\AA}^3$, $K_0=37.6(2.1)\text{ GPa}$, $K'=7.9(1.5)$] and for Sr(OH)₂ [$V_0=236.32(3)\text{\AA}^3$, $K_0=27.6(1.3)\text{ GPa}$, $K'=14.4(1.4)$]. The very high value of K' indicates another low-P phase transition in the Sr(OH)₂ system. At pressures above 10 GPa Sr(OH)₂ starts to amorphize.

Literature:

[1] Cordfunke E.H.P. *et al.* "A study of the phase transitions in Ba(OH)₂ and a comment on the fusion of Sr(OH)₂.", *Thermochimica Acta*, (1996), 273: 1 - 9.

[2] Friedrich, A. *et al.* (2000) 19th European Crystallographic Meeting, Nancy, France.