	Experiment title: The phase diagram of CaC$_2$	**Experiment number:** CH-5062
Beamline: BM25A	**Date of experiment:** from: 03.03.2017 to: 08.03.2017	**Date of report:** 08.02.2018
Shifts: 12	**Local contact(s):** A. Serrano	*Received at ESRF:*

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Report:

Despite the fact that calcium carbide, CaC$_2$, is an important commodity chemical with a world-wide production of almost 10 million tons per year (2005), its phase diagram is still not completely understood. Although *Bredig* presented a phase diagram already in 1942 that was accepted for a long time,[1] and the crystal structures of all four modifications of CaC$_2$ were known since our work in 2001,[2] there was some doubt about important details of this phase diagram.[3-6] Therefore, we proposed a revision of *Bredig*'s diagram, which is shown in Figure 1 (left).
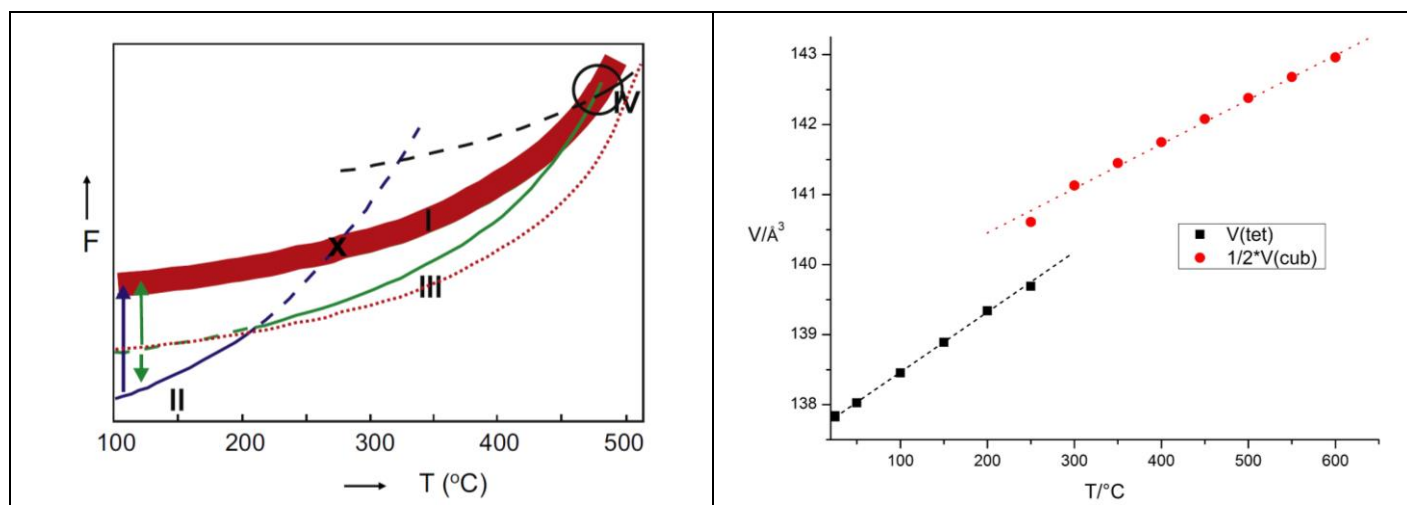

Figure 1: left: revised phase diagram of CaC$_2$ as proposed by *Häussermann*, *Ruschewitz* and co-workers in Ref. 5; right: unit cell volume of BaC$_2$ (prepared from Ba:C = 1:2) in dependence of the temperature (tet: *I4/mmm*, Z = 2; cub: *Fm-3m*, Z = 4). Broken lines are linear regression fits to the data (BM25A) of the unit cell volume of the tetragonal and cubic modifications, respectively.

To validate this proposed phase diagram mainly the following questions need to be answered:

(i) Is CaC_2 really a one-component system, i.e. do all modifications have the stoichiometric composition CaC_2?

(ii) How does the Ca:C ratio influence the ratio of the different modifications being formed?

(iii) In which way do the different modifications I-IV transform to each other?

(iv) What is the nature of disorder in CaC_2-IV, from which all other modifications are obviously formed upon cooling?

All these questions were addressed in the current (CH-5062) and a former beamtime (CH-4646) by temperature-dependent synchrotron powder diffraction measurements on samples prepared from different Ca:C ratios (1:1.8, 1:2, 1:2.2). As the phase diagrams of SrC_2 and BaC_2 are similar, but somewhat simpler than that of CaC_2 (the proposed metastable modification III is not known for them),[2] these alkaline earth metal acetylides were also included in these investigations. With respect to question (i) we found that within the precision possible at beamlines BM01B and BM25A all compounds prepared from different metal:C ratios give essentially the same lattice parameters* so that it must be concluded that they are "stoichiometric" compounds with the ideal composition AEC_2 with $AE = Ca^{2+}$, Sr^{2+}, Ba^{2+} (cp. Table 1) and no phase width.

*Note: It is well-known and accepted that the esd's obtained from a Rietveld refinement are underestimated by a factor of at least 3.

	Beamline	AE:C ratio	a/Å	c/Å	V/Å^3
CaC_2	BM01B	1:1.8	3.8858(9)	6.388(3)	96.45(6)
		1:2	3.886(1)	6.394(3)	96.55(7)
		1:2.2	3.885(1)	6.392(5)	96.47(9)
SrC_2	BM01B	1:1.8	4.11311(6)	6.7652(1)	114.451(6)
		1:2	4.11156(8)	6.7650(2)	114.362(7)
		1:2.2	4.11098(4)	6.76550(9)	114.338(3)
BaC_2	BM25A	1:1.8	4.3978(1)	7.1190(3)	137.69(1)
		1:2	4.4000(8)	7.1190(2)	137.823(7)
		1:2.2	4.39872(8)	7.1200(2)	137.763(8)

Table 1: Lattice parameters of tetragonal modifications I ($I4/mmm$, $Z = 2$, 295 K) in AEC_2 with $AE = Ca^{2+}$, Sr^{2+}, Ba^{2+} depending upon the ratio AE:C used for their synthesis.

For the disorder of C_2 dumbbells in the cubic high-temperature modifications of CaC_2, SrC_2, and BaC_2 an isotropic free rotation (Pauling model) and a random exchange process between distinct directions consistent with cubic symmetry (Frenkel model) are possible. The high-temperature behavior in the stability regime of the cubic modification (cp. Figure 1, right) reveals that the unit cell volumes increase almost linearly with increasing temperature, i.e. there is no kink in the curve that would indicate a transition from a Frenkel model to a Pauling model. This is an important finding to answer question (iv).

The evaluation of the collected data to answer questions (ii) and (iii) is still under way.

References

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