Acta Crystallographica Section B
Structural Science
ISSN 0108-7681

Synthesis and characterization of the barium oxalates $BaC_2O_4{\cdot}0.5H_2O$, α-BaC_2O_4 and β-BaC_2O_4

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Received 20 July 2001
Accepted 3 December 2001

The synthesis of $BaC_2O_4{\cdot}0.5H_2O$ and its thermal decomposition to α-BaC_2O_4 and β-BaC_2O_4 was investigated. $BaC_2O_4{\cdot}0.5H_2O$ is precipitated at room temperature from aqueous solutions of barium chloride and ammonium oxalate. The deuterated compound $BaC_2O_4{\cdot}0.5D_2O$ was made in analogy with D_2O as the solvent. The compounds were characterized by X-ray and neutron diffraction analysis. Single-crystal X-ray diffraction of $BaC_2O_4{\cdot}0.5H_2O$ measured at 120 K gave the triclinic cell $a = 8.692$ (1), $b = 9.216$ (1), $c = 6.146$ (1) Å, $\alpha = 95.094$ (3), $\beta = 95.492$ (3), $\gamma = 64.500$ (3)°, space group $P\bar{1}$, $Z = 4$. Two independent Ba atoms are each coordinated to nine O atoms at distances from 2.73 (1) to 2.99 (1) Å. One of the two oxalate ions deviates significantly from planarity. The water molecule does form weak hydrogen bonds. *In situ* X-ray powder diffraction was used to study the thermal decomposition of $BaC_2O_4{\cdot}0.5H_2O$ and the formation of α-BaC_2O_4. The X-ray powder pattern of α-BaC_2O_4 measured at 473 K was indexed on a triclinic cell with $a = 5.137$ (3), $b = 8.764$ (6), $c = 9.006$ (4) Å, $\alpha = 83.57$ (4), $\beta = 98.68$ (5), $\gamma = 99.53$ (5)°, and the space group $P\bar{1}$ with $Z = 4$.

1. Introduction

Barium oxalate forms four hydrates, of which hydrogen bonds have been studied of $BaC_2O_4{\cdot}3.5D_2O$ (Neder *et al.*, 1997), $BaC_2O_4{\cdot}2D_2O$ (Christensen *et al.*, 1995) and $BaC_2O_4{\cdot}D_2O$ (Christensen, 1992) by neutron powder diffraction analysis. The crystal structure of the barium oxalate hemihydrate $BaC_2O_4{\cdot}0.5H_2O$ (Mutin *et al.*, 1981) has been studied by single-crystal X-ray diffraction analysis. Hydrogen bonds were not investigated. Two modifications of the anhydrous compound BaC_2O_4 (Walter-Levy & Laniepce, 1965) have been reported. The present study was made to complete the description of hydrogen bonding in barium oxalates and to characterize anhydrous barium oxalate.

2. Experimental

2.1. Chemistry

Barium chloride, $BaCl_2{\cdot}2H_2O$ (Merck p.a.), and ammonium oxalate, $(NH_4)_2C_2O_4{\cdot}H_2O$ (Merck p.a.), were used in the synthesis. $BaC_2O_4{\cdot}0.5H_2O$ was obtained when 500 ml of a 0.2 *M* solution of $BaCl_2{\cdot}2H_2O$ was added dropwise at room temperature to 500 ml of a 0.2 *M* solution of $(NH_4)_2C_2O_4{\cdot}H_2O$. The white crystalline product of $BaC_2O_4{\cdot}0.5H_2O$ was washed with water, filtered and dried at room temperature. The deuterated compound $BaC_2O_4{\cdot}0.5D_2O$ was made in a similar way using 99.99% D_2O (Norsk Hydro) as the solvent.

Recrystallization and crystal growth of $BaC_2O_4{\cdot}0.5H_2O$ was investigated by hydrothermal synthesis in the temperature range 403–498 K. Approximately 7 g of $BaC_2O_4{\cdot}0.5H_2O$ was heated with 175 ml water for 80 h. The reaction product was $BaC_2O_4{\cdot}0.5H_2O$. The hydrothermal treatments did not improve the crystal quality and size of the crystals. Hydrothermal synthesis made at 593 K resulted in the formation of $BaCO_3$. Larger crystals of $BaC_2O_4{\cdot}0.5H_2O$ were made by slow mixing of a barium chloride and an ammonium oxalate solution in a diffusion mode, as described elsewhere (Christensen *et al.*, 1991).

Differential thermal analysis and thermogravimetric analysis of $BaC_2O_4{\cdot}0.5H_2O$ were performed in the temperature range 293–746 K using a Stanton Redcroft TG-DTA simultaneous thermal analyzer STA 1000/1500 using a heating rate of 5 K min^{-1} and Ar gas flow on the sample. The dehydration to α-BaC_2O_4 takes place in the temperature interval 383–418 K and the loss in weight of 3.0% corresponds to the formation of the anhydrous compound, see Fig. 1 (calculated value 3.8%). A phase transition from α-BaC_2O_4 to β-BaC_2O_4 was reported to take place at approximately 663 K (Walter-Levy & Laniepce, 1965) and β-BaC_2O_4 was only stable in a narrow temperature range before the compound decomposed to $BaCO_3$. The heating was interrupted, see Fig. 1, when α-BaC_2O_4 started to lose weight and an X-ray powder pattern of the sample had reflections of β-BaC_2O_4, α-BaC_2O_4 and $BaCO_3$.

The thermal decomposition of $BaC_2O_4{\cdot}0.5D_2O$ was also investigated in the temperature range 373–753 K in gravimetric analyses where samples of the compound placed in Pt crucibles were heated in an electric furnace for up to 15 h. The temperature in the furnace was measured with a Pt–Pt 13% Rh thermocouple. The loss in weight in the temperature range 633–753 K is displayed in Fig. 2. The sample was only dried at room temperature and the observed loss in weight exceeds the loss of $BaC_2O_4{\cdot}0.5D_2O$ to $BaCO_3$, which is 16.2%. Powder patterns were taken of the samples after the heat treatments to identify the decomposition products (see below) and had reflections of β-BaC_2O_4, α-BaC_2O_4 and $BaCO_3$.

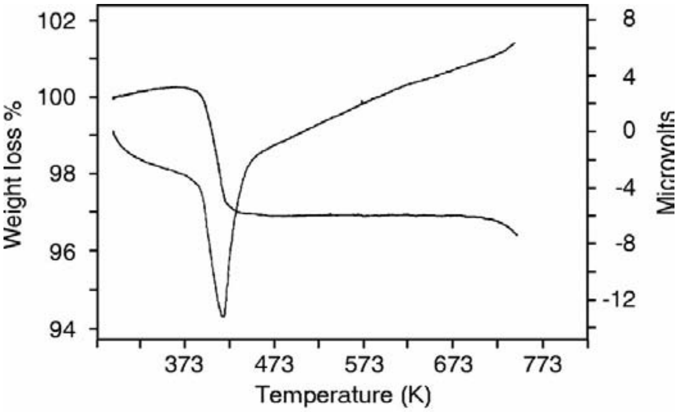

Figure 1
DTA and TGA diagrams for the dehydration of $BaC_2O_4{\cdot}0.5H_2O$ to α-BaC_2O_4. The dehydration takes place in the temperature interval 383–418 K.

The IR spectrum of $BaC_2O_4{\cdot}0.5H_2O$ was measured on a Perkin-Elmer Paragon 1000 FT-IR spectrometer. An absorption at 3500 cm^{-1} indicates that there are no strong hydrogen bonds with short bond distances in the structure.

2.2. X-ray and neutron powder diffraction

The purity of the synthesized products was tested with X-ray diffraction powder patterns measured on a Stoe-Stadi powder diffractometer using Cu $K\alpha_1$ radiation (λ = 1.5406 Å). A transmission mode was applied with a flat sample on tape. The diffractometer was calibrated with an external silicon standard ($a_{\rm Si}$ = 5.43050 Å). The counter was a curved position-sensitive detector covering 40° in 2θ or a linear detector covering 5° in 2θ and used in a step scan mode. The X-ray powder patterns of the samples used in the thermal decomposition of $BaC_2O_4{\cdot}0.5D_2O$ were measured on a Philips diffractometer using Co $K\alpha_1$ (λ = 1.7889 Å).

Synchrotron X-ray powder diffraction patterns of $BaC_2O_4{\cdot}0.5H_2O$ were measured on the powder diffractometer at the beamline X7A at NSLS, Brookhaven National Laboratory. The sample was kept in a 0.2 mm-diameter quartz glass capillary, which was rotated at 50 r.p.m. to randomize the crystallites. A neutron diffraction powder pattern of $BaC_2O_4{\cdot}0.5D_2O$ was measured at the diffractometer D1A at the Institute Max von Laue–Paul Langevin. The experimental data for the measured powder patterns are listed in Table 1.

2.3. *In situ* study of the $BaC_2O_4{\cdot}0.5H_2O$ decomposition

The decomposition of $BaC_2O_4{\cdot}0.5H_2O$ to α-BaC_2O_4 was investigated by time-resolved X-ray powder diffraction using an INEL diffractometer with a position-sensitive detector

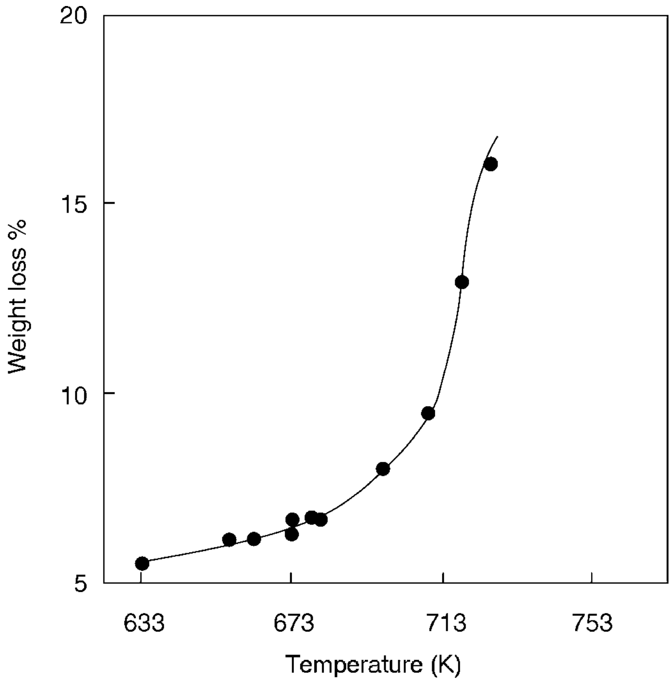

Figure 2
Loss in weight of $BaC_2O_4{\cdot}0.5D_2O$ *versus* temperature. *Ex situ* investigations. Each point represents a sample kept at the temperature for 8–12 h.

Table 1
Experimental data for the measured powder patterns of $BaC_2O_4{\cdot}0.5H_2O$ (I), $BaC_2O_4{\cdot}0.5D_2O$ (II) and BaC_2O_4 (III).

Sample	(I)	(I)	(I)	(II)	(III)	(III)	(III)	(III)
Powder pattern	A	B	C	D	E	F	G	H
Diffractometer	Stoe-Stadi	INEL CSIRO	X7A NSLS	D1A ILL	Stoe-Stadi	Philips CSIRO	INEL CSIRO	Philips
Radiation	Cu $K\alpha_1$	Cu $K\alpha_{1,2}$	Synchrotron	Neutron	Cu $K\alpha_1$	Cu $K\alpha_{1,2}$	Cu $K\alpha_{1,2}$	Cu $K\alpha_1$
$2\theta_{min}$ (°)	1.00	1.00	8.00	12.00	10.00	8.00	1.00	8.00
$2\theta_{max}$ (°)	70.00	121.00	74.00	152.00	70.00	50.00	121.00	58.00
$\Delta 2\theta$ (°)	0.02	0.03	0.01	0.05	0.02	0.02	0.03	0.02
λ (Å)	1.5406	1.5418	1.3150	1.9090	1.5406	1.5418	1.5418	1.7889
Max sin θ/λ (Å^{-1})	0.472	0.564	0.458	0.508	0.372	0.274	0.564	0.271
Flat plate	Yes	Yes			Yes	Yes	Yes	Yes
Capillary 0.2 mm			Yes					
V container				Yes				
Diameter (cm)				12				
Rotation of sample (r.p.m.)	60		60		60			
Temperature (K)	298	298	298	298	298	473	393	298

Table 2
Experimental data and unit-cell parameters for the low-temperature single-crystal measurement of $BaC_2O_4{\cdot}0.5H_2O$.

a (Å)	8.692 (1)
b (Å)	9.216 (1)
c (Å)	6.146 (1)
α (°)	95.094 (3)
β (°)	95.492 (3)
γ (°)	64.500 (3)
Cell volume (Å^3)	441.7
Space group	$P\bar{1}$
Z	4
Density (calc) (g cm^{-3})	3.45
Size of crystal (mm)	0.01 × 0.06 × 0.15
Linear absorption coefficient, μ (mm^{-1})	9.0
No. of measured reflections	6475
No. of independent reflections with $I > 3\sigma(I)$	1339
$R(F)$	0.049
T (K)	120

covering a 2θ range of 120° and with a Philips X'Pert diffractometer using a step scan mode. The flat sample holder on each of the diffractometers was a platinum plate which was also the heating element, controlled by an Anton Paar HTK2-HC temperature controller. A Pt–Pt 10% Rh thermocouple was welded to the back of the sample holder. The powder samples were mixed with acetone and the mixture was placed on the sample holder with a pipette. The powder sample proved to have excellent contact with the sample holder, resulting in only a small temperature gradient between sample, heater (sample holder) and thermocouple. The samples were housed in a vacuum chamber with Mylar windows at a pressure of approximately 10 torr. The diffractometers were calibrated with an external standard of Y_2O_3 and temperature calibration was made with a sample of KNO_3, which showed the α–β transition of the compound on heating at 403 K. This is in acceptable agreement with the reported transition temperatures 401 and 402 K, respectively (Christensen *et al.*, 1996; Weast *et al.*, 1987). At this pressure the decomposition temperature of $BaC_2O_4{\cdot}0.5H_2O$ to α-BaC_2O_4 was 370 (3) K. The magnitude of the temperature gradient of the sample exposed by the X-ray beam is not known.

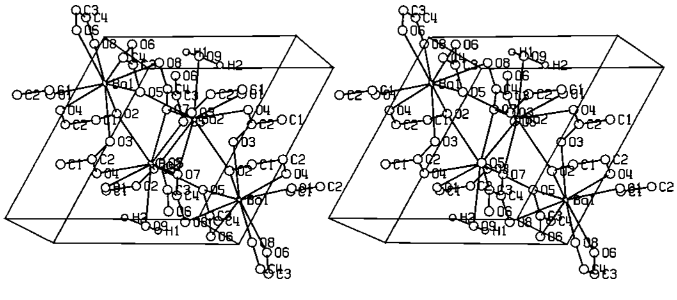

Figure 3
Stereoscopic view of the structure of $BaC_2O_4{\cdot}0.5H_2O$ along [001].

2.4. X-ray single-crystal diffraction of $BaC_2O_4{\cdot}0.5H_2O$

Single-crystal diffraction data were measured at 120 K on a Siemens SMART diffractometer with an area detector, using Mo $K\alpha$ radiation (λ = 0.7107 Å). Experimental and crystallographic data are listed in Table 2.[1] The direct-method program *SIR* (Altomare *et al.*, 1994) gave the positions of all the atoms in the structure of $BaC_2O_4{\cdot}0.5H_2O$ and a final Fourier map did not show any additional electron density. The structure was refined with the least-squares program *LINUS* (*LINUS* is the 1971 version of *ORFLS*; Busing *et al.*, 1962) with scattering contributions from neutral atoms (Cromer & Waber, 1964) and corrections for anomalous scattering contributions for the Ba atom (MacGillavry *et al.*, 1962). Absorption corrections were applied (Busing *et al.*, 1962). Atomic coordinates and thermal displacement parameters are given in Table 3 and some interatomic distances are given in Table 4. A stereoscopic view of the structure along [001] with the *a* axis across the page is displayed in Fig. 3.

3. Analysis of $BaC_2O_4{\cdot}0.5H_2O$ single-crystal diffraction data

The two Ba atoms are coordinated to nine O atoms with bonds from 2.73 (1) to 2.99 (1) Å, and 2.73 (1) to 2.91 (1) Å,

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[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS0083). Services for accessing these data are described at the back of the journal.

Table 3
Positional parameters for the structure of $BaC_2O_4{\cdot}0.5H_2O/D_2O$.

For each atom are listed: first line: refined parameters from X-ray single-crystal data; second line: EXPO solution from pattern C; third line: EXPO solution from pattern D; fourth line: refined parameters neutron diffraction powder pattern D.

	x	*y*	*z*
Ba1	0.9558 (1)	0.2093 (1)	0.2782 (1)
	0.964	0.207	0.284
	–	–	–
	0.965 (2)	0.206 (2)	0.273 (3)
Ba2	0.3635 (1)	0.4185 (1)	0.2132 (1)
	0.367	0.415	0.207
	–	–	–
	0.369 (2)	0.422 (2)	0.206 (3)
C1	0.923 (2)	0.676 (2)	0.176 (3)
	0.869	0.675	0.127
	0.906	0.623	0.152
	0.908 (2)	0.662 (2)	0.190 (3)
C2	0.819 (2)	0.626 (2)	0.324 (3)
	0.840	0.638	0.340
	0.834	0.663	0.335
	0.815 (2)	0.632 (2)	0.313 (3)
O1	0.874 (1)	0.686 (1)	−0.020 (2)
	0.900	0.676	−0.001
	0.864	0.708	0.006
	0.881 (3)	0.683 (3)	−0.026 (3)
O2	1.048 (1)	0.696 (1)	0.267 (2)
	1.031	0.765	0.314
	1.029	0.757	0.293
	1.052 (2)	0.693 (2)	0.269 (3)
O3	0.747 (1)	0.540 (1)	0.239 (2)
	0.745	0.559	0.275
	0.784	0.554	0.256
	0.736 (2)	0.546 (2)	0.244 (3)
O4	0.818 (2)	0.673 (1)	0.525 (2)
	0.797	0.672	0.527
	0.767	0.670	0.404
	0.813 (2)	0.670 (2)	0.534 (3)
C3	0.276 (2)	0.821 (2)	0.135 (2)
	0.309	0.797	0.175
	0.309	0.833	0.082
	0.276 (2)	0.818 (2)	0.133 (3)
C4	0.287 (2)	0.816 (2)	0.385 (3)
	–	–	–
	0.334	0.805	0.327
	0.279 (2)	0.812 (2)	0.390 (3)
O5	0.356 (1)	0.690 (1)	0.028 (2)
	0.335	0.688	0.062
	0.372	0.734	−0.028
	0.360 (2)	0.683 (2)	0.020 (2)
O6	0.185 (1)	0.950 (1)	0.050 (2)
	0.184	0.936	0.027
	0.216	0.959	0.027
	0.181 (3)	0.953 (2)	0.030 (3)
O7	0.370 (1)	0.685 (1)	0.474 (2)
	0.359	0.694	0.478
	–	–	–
	0.369 (2)	0.678 (2)	0.478 (3)
O8	0.199 (1)	0.947 (1)	0.487 (2)
	0.215	0.911	0.481
	–	–	–
	0.204 (2)	0.946 (2)	0.485 (3)
O9	0.516 (2)	0.070 (1)	0.221 (2)
	0.548	0.054	0.193
	0.438	0.091	0.287
	0.500 (3)	0.082 (3)	0.210 (4)
H1	0.58	0.04	0.24
	–	–	–
	–	–	–
	0.615 (5)	0.035 (5)	0.282 (6)
H2	0.45	0.08	0.15
	–	–	–
	–	–	–
	0.488 (6)	0.076 (6)	0.110 (5)
H2′	–	–	–
	–	–	–
	–	–	–
	0.409 (5)	0.104 (5)	0.315 (8)

respectively, and in deformed prisms similar to the coordination polyhedra in the structures of $BaC_2O_4{\cdot}3.5D_2O$ (Neder *et al.*, 1997). One of the two oxalate ions deviates significantly from planarity. The distances to the best plane through the six atoms of the oxalate ion containing the atoms C1, C2 and O1–O4 are: C1 −0.02, C2 −0.01, O1 −0.27, O2 0.28, O3 0.28, O4 −0.27 Å. The deviation from planarity of this oxalate ion is thus significant. The distances to the best plane through the atoms of the oxalate ion containing the atoms C3, C4 and O5–O8 are: C3 −0.02, C4 −0.03, O5 0.01, O6 0.02, O7 0.02, O8 0.01 Å. The deviation from planarity of this oxalate ion is marginal. The water molecule with the atoms O9, H1 and H2 does take part in a hydrogen bond where the bond distance O9—O8 is 2.88 (2) Å.

4. Analysis of powder diffraction patterns

4.1. $BaC_2O_4{\cdot}0.5H_2O$: test of structure solution from X-ray powder diffraction data

Unit-cell parameters and space groups for the barium oxalate hydrates and the anhydrous barium oxalate are listed in Table 5. The X-ray diffraction powder pattern of $BaC_2O_4{\cdot}0.5H_2O$, Table 1, C, was indexed with the program *FZON* (Visser, 1969) on a triclinic cell. This cell is different from that of Mutin *et al.* (1981), but that unit cell can be converted to the unit cell of this work by the matrix

$$\begin{matrix} -1 & -1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & -1 \end{matrix}$$

and this is also the cell used on the ICDD card No. 20-134 and in the single-crystal structure analysis above. The powder pattern was decomposed by the program *ALLHKL* (Pawley, 1981) giving an *R* value of 0.091 for each of the two unit cells. A structure solution was obtained using the direct-method program *EXPO* (Altomare *et al.*, 1995). The results of the structure solution are given in Table 3. The two Ba atoms were found in excellent agreement with the results of the single-crystal data analysis and only three atoms, C4, H1 and H2, could not be located. A synchrotron X-ray powder diffraction pattern can thus give an almost complete crystal structure even in the case of a heavy-atom structure.

4.2. $BaC_2O_4{\cdot}0.5D_2O$: structure solution from neutron diffraction powder data

The average scattering contribution from the Ba, C, O and D atoms are in the neutron diffraction case 8.8, 28.5, 48.9 and

Table 4
Interatomic distances (in Å) of $BaC_2O_4{\cdot}0.5H_2O$.

X-ray single-crystal data and positional parameters for H atoms from profile refinement of neutron powder diffraction data. Symmetry operations give positions of the O atoms with reference to the positions listed in Table 4.

Ba1—O6^{i}	2.73 (1)	Ba2—O5^{ii}	2.73 (1)
Ba1—O1^{iii}	2.75 (1)	Ba2—O7^{iv}	2.75 (1)
Ba1—O8^{i}	2.76 (1)	Ba2—O1^{ii}	2.76 (1)
Ba1—O4^{v}	2.77 (1)	Ba2—O4^{iv}	2.77 (1)
Ba1—O3	2.82 (1)	Ba2—O5	2.81 (1)
Ba1—O2^{v}	2.85 (1)	Ba2—O7	2.83 (1)
Ba1—O6^{ii}	2.88 (1)	Ba2—O2^{vi}	2.85 (1)
Ba1—O8^{iv}	2.90 (1)	Ba2—O3^{ii}	2.86 (1)
Ba1—O5^{ii}	2.99 (1)	Ba2—O9	2.91 (1)
C1—O1	1.24 (2)	C3—O5	1.26 (2)
C1—O2	1.25 (2)	C3—O6	1.25 (2)
C2—O3	1.25 (2)	C4—O7	1.25 (2)
C2—O4	1.27 (2)	C4—O8	1.27 (2)
C1—C2	1.56 (2)	C3—C4	1.53 (2)
O9—H1	0.70 (11)		
O9—H2	0.95 (15)		
O9—O8^{iv}	2.88 (2) (hydrogen bond)		
O9—O9	2.90 (3)		

Symmetry codes: (i) $1+x, y-1, z$; (ii) $2-x, 1-y, -z$; (iii) $2-x, 1-y, 1-z$; (iv) $1-x, 1-y, -z$; (v) $1-x, 1-y, 1-z$; (vi) $x-1, y, z$.

13.8%, respectively. The neutron diffraction powder pattern, Table 1, D, was used with the direct method program *EXPO* (Altomare *et al.*, 1995) in a structure solution and the results are given in Table 3. The atoms Ba1, Ba2, O7, O8, H1(D1) and H2(D2) were not found. The initial positions of the D atoms of $BaC_2O_4{\cdot}0.5D_2O$ were derived from the single-crystal investigation and the model of the structure was refined using the least-squares program *DBW*3.2*S* (Wiles *et al.*, 1988). Positional parameters are given in Table 3 and are in acceptable agreement with the positional parameters found in the single-crystal X-ray diffraction analysis. The water molecule forms weak hydrogen bonds in the structure. The atom H1(D1) is part of the O9—O8 hydrogen bond of 2.88 (2) Å. The O9—O9 distance over a center of symmetry of 2.90 (3) Å indicates that the H atom of the water molecule H2(D2) must be placed statistically in two sites, as indicated in Table 3.

4.3. α-BaC_2O_4

The solid-state decomposition of $BaC_2O_4{\cdot}0.5H_2O$ to BaC_2O_4 results readily in the formation of the α-BaC_2O_4 modification, but the β-BaC_2O_4 modification may also be obtained. α-BaC_2O_4 can absorb water so that $BaC_2O_4{\cdot}0.5H_2O$ is formed. It is thus a challenge to make a pure sample of α-BaC_2O_4 and β-BaC_2O_4 and powder patterns of α-BaC_2O_4 stored for a few days often show $BaC_2O_4{\cdot}0.5H_2O$ as an impurity. The patterns, Table 1, G and F, were recorded in the *in situ* experiments with the INEL and Philips diffractometers and gave patterns of α-BaC_2O_4 without β-BaC_2O_4 and $BaC_2O_4{\cdot}0.5H_2O$ as impurities.

Assuming a linear relation of the volume of one formula unit of the barium oxalate hydrates $BaC_2O_4{\cdot}xH_2O$ *versus* x ($x = \frac{1}{2}$, 1, 2 and 3.5), the volume of one formula unit of BaC_2O_4 would be approximately 100 Å^3. The powder pattern, Table 1, F, of α-BaC_2O_4 was indexed with the program *DICVOL* (Boultif & Louër, 1991) on a triclinic cell with a volume of 393 Å^3, in agreement with the expected volume of four BaC_2O_4 formula units.

Pattern F was decomposed by the program *ALLHKL* (Pawley, 1981) giving an R value of 7.0%. The indexed powder pattern of α-BaC_2O_4 is listed in Table 6. The reflection with d = 2.715 Å is in different patterns observed with different intensities and is possibly due to an impurity. With this reflection omitted pattern F could also be decomposed with *ALLHKL* (Pawley, 1981), giving an R value of 0.073 and a unit cell with half the volume of that reported above. This corresponds to four or two formula units of α-BaC_2O_4 in the two cells, respectively. The indexed powder pattern, Table 6, has almost all reflection with $l = 2n$, and the first observed low-angle reflection of α-BaC_2O_4 is at d = 5.014 Å, in contrast to the first observed low-angle reflection of $BaC_2O_4{\cdot}0.5H_2O$ at d = 8.360 Å. This could support the hypothesis that the unit-cell volume of α-BaC_2O_4 was half that of $BaC_2O_4{\cdot}0.5H_2O$ and thus has a volume of 197 Å^3 with the unit-cell parameters a = 5.137 (3), b = 8.764 (7), c = 4.503 (5) Å, α = 83.57 (4), β = 98.68 (5), γ = 99.53 (5)°. The two cells were used in attempts to solve the structure of α-BaC_2O_4 from the X-ray

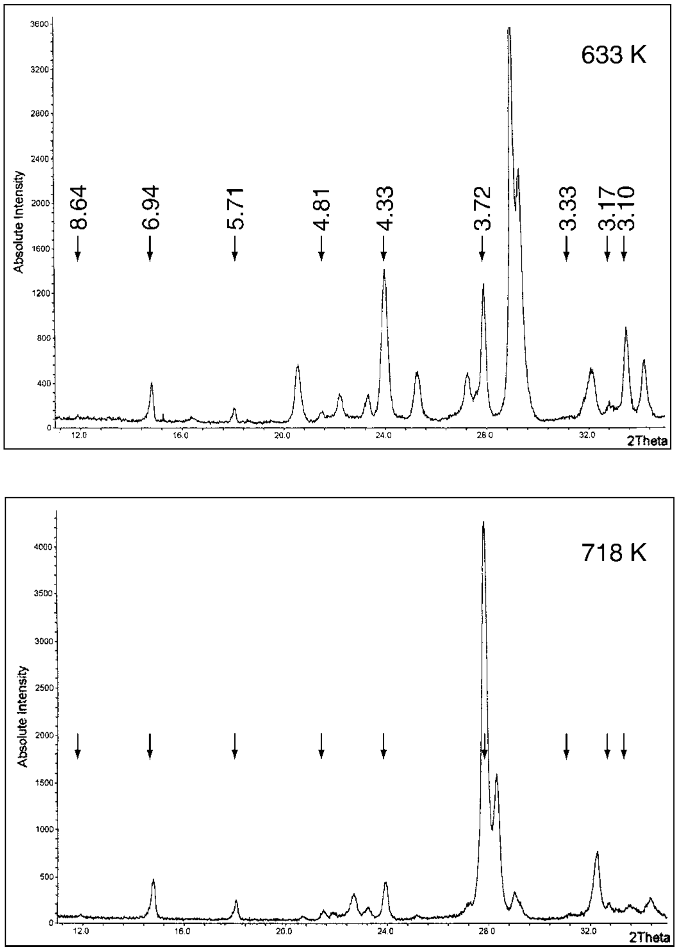

Figure 4
Powder patterns of samples kept at 633 and 718 K, respectively. Reflections marked with arrows are from β-BaC_2O_4. Other reflections are from α-BaC_2O_4 (633 K pattern) and from $BaCO_3$ (718 K pattern).

Table 5
Unit-cell parameters and space groups for the barium oxalate hydrates and for anhydrous barium oxalate.

Powder pattern: the capital letters refer to the patterns listed in Table 2.

	a	*b*	*c*	α	β	γ	Space group	Ref./ICDD	Powder pattern
$BaC_2O_4{\cdot}3.5D_2O$	13.489 (1)	7.663 (19)	15.085 (1)		113.57 (1)		$C2/c$	1	
$BaC_2O_4{\cdot}2D_2O$	7.538 (1)	11.062 (1)	7.105 (1)		105.42 (1)		$P2_1/c$	2	
$BaC_2O_4{\cdot}D_2O$	10.0648 (3)	7.9350 (2)	6.8503 (2)		122.35 (2)		$C2/m$	3	
$BaC_2O_4{\cdot}0.5D_2O$	9.312 (1)	9.649 (1)	6.188 (1)	90.13 (2)	95.36 (2)	125.18 (2)	$P\bar{1}$	4	
$BaC_2O_4{\cdot}0.5D_2O$	8.748	9.298	6.170	94.91	95.48	64.19	$P\bar{1}$	20–134	
$BaC_2O_4{\cdot}0.5D_2O$	8.751 (1)	9.308 (1)	6.172 (1)	94.98 (1)	95.51 (1)	64.16 (1)	$P\bar{1}$	This work	C
$BaC_2O_4{\cdot}0.5D_2O$	8.684 (2)	9.241 (2)	6.153 (2)	95.55 (2)	95.53 (2)	64.43 (2)	$P\bar{1}$	This work	D†
α-BaC_2O_4	5.137 (3)	8.764 (6)	9.006 (4)	83.57 (4)	98.68 (5)	99.53 (5)	$P\bar{1}$	This work	F
β-BaC_2O_4	8.71 (2)	6.99 (2)	9.91 (3)	89.4 (2)	96.0 (2)	92.9 (2)	$P\bar{1}$	19–125	

† The unit-cell dimensions derived from pattern D are approximately 0.5% smaller than those for pattern C, which possibly indicates that the neutron wavelength is underestimated by 0.5%.

Table 6
Indexed powder pattern of α-BaC_2O_4.

The observed intensities derived in a profile fit to the pattern using the program *ALLHKL* (Pawley, 1981).

$2\theta_{obs}$ (°)	$2\theta_{calc}$ (°)	d_{obs} (Å)	d_{calc} (Å)	I_{obs}	*hkl*
17.67	17.65	5.014	5.020	47	100
19.07	19.09	4.651	4.646	4	$10\bar{1}$
	19.06		4.654		$1\bar{1}0$
19.97	19.93	4.443	4.451	15	$1\bar{1}\bar{1}$
	20.01		4.434		002
20.60	20.62	4.307	4.304	53	020
21.68	21.69	4.095	4.093	52	012
23.33	23.36	3.810	3.806	20	$01\bar{2}$
24.89	24.91	3.575	3.571	85	$10\bar{2}$
25.11	25.11	3.543	3.543	100	$1\bar{2}0$
27.54	27.54	3.236	3.236	29	022
28.66	28.64	3.112	3.114	23	$1\bar{2}1$
29.29	29.28	3.047	3.048	23	120
30.16	30.13	2.961	2.964	7	$1\bar{1}2$
	30.18		2.959		$02\bar{2}$
30.77	30.76	2.903	2.905	23	112
32.96	32.93	2.715	2.718	8	$1\bar{1}\bar{3}$
34.98	34.96	2.563	2.565	6	$1\bar{2}2$
35.40	35.40	2.533	2.534	38	$12\bar{2}$
36.03	36.04	2.491	2.490	8	122
38.17	38.17	2.356	2.356	4	$2\bar{1}\bar{2}$
38.63	38.67	2.329	2.327	45	$2\bar{2}0$
38.86	38.85	2.316	2.316	15	$03\bar{2}$
	38.83		2.317		210
40.51	40.50	2.225	2.225	2	$2\bar{2}\bar{2}$
41.09	41.10	2.195	2.195	3	014
41.83	41.84	2.158	2.158	17	033
42.07	42.07	2.146	2.146	14	$1\bar{3}2$
43.00	43.00	2.102	2.102	16	$1\bar{2}3$
	43.00		2.102		$01\bar{4}$
	43.00		2.102		123

Triclinic cell $a = 5.137$ (3), $b = 8.714$ (6), $c = 9.006$ (4) Å, $\alpha = 83.57$ (4), $\beta = 98.68$ (5), $\gamma = 99.53$ (5)°, $M(25) = 12.6$.

powder patterns. The program *EXPO* (Altomare *et al.*, 1995) was used and yielded solutions with positions of the heavy Ba atoms. None of these could give calculated intensities of the models in sufficient agreement with the observed intensities, using the powder patterns Table 1, F and H. These patterns had much higher intensities of the observed reflections in the 2θ ranges 24.5–25.3 (pattern F) and 28.0–30.0 (pattern H) than the calculated intensities from the models. The powder patterns available were thus not sufficiently resolved. Synchrotron X-ray diffraction patterns would be necessary for a solution of the structure of α-BaC_2O_4.

4.4. β-BaC_2O_4

In the synthesis of barium oxalate from $BaC_2O_4{\cdot}0.5H_2O$ and $BaC_2O_4{\cdot}0.5D_2O$, β-BaC_2O_4 was only obtained as an impurity phase. Samples of $BaC_2O_4{\cdot}0.5D_2O$ kept in the temperature range 633–718 K (Fig. 2) had reflections of β-BaC_2O_4, α-BaC_2O_4 and $BaCO_3$ in their powder patterns. Fig. 4 displays a 2θ range of the powder pattern of two samples kept at 633 and 718 K, respectively. The pattern of the sample kept at 633 K has strong reflections of α-BaC_2O_4 and reflections of β-BaC_2O_4 marked with arrows and *d*-spacing values which are in agreement with the values listed for β-BaC_2O_4 in the ICDD database card No. 19-125. The pattern of the sample kept at 718 K has strong reflections of $BaCO_3$ and also reflections of β-BaC_2O_4. The compound β-BaC_2O_4 can thus coexist both with α-BaC_2O_4 and with $BaCO_3$, and it is formed in a temperature range where the loss in weight of barium oxalate is increasing (Fig. 2). The strong β-BaC_2O_4 reflection at $d = 3.72$ Å has the same position as the strong reflection of $BaCO_3$ at 3.722 Å.

The Danish Natural Science Research Council has supported this investigation with grants. The instrument for DTA-TGA was obtained with a grant from *Carlsbergfondet*. The National Synchrotron Light Source, Brookhaven National Laboratory, Upton, NY, and Institut Max von Laue–Paul Langevin, Grenoble, are acknowledged for the use of the powder diffractometers. Mrs C. Secher, Mrs M. A. Chevallier and Mr N. J. Hansen are thanked for valuable assistance.

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