Crystal structure, polymorphism and anisotropic thermal expansion of α-$Ca(CH_3COO)_2$ - Supporting Information

Sebastian Bette[a b e,], Gerhard Eggert[b], Sebastian Emmerling[a,c], Martin Etter[d], Thomas Schleid[e], Robert E. Dinnebier[a]*

AUTHOR ADDRESSES

[a]Max Planck Institute for Solid State Research, Heisenbergstr. 1, 70569 Stuttgart, Germany

[b]State Academy of Art and Design, Am Weißenhof 1, 70191 Stuttgart, Germany

[c]Department of Chemistry, Ludwig Maximilian University of Munich, Butenandtstr. 5-13, 81377 Munich, Germany

[d]Deutsches Elektronen-Synchtrotron (DESY), Notkestraße 85, 22607 Hamburg, Germany

[e]Institute for Inorganic Chemistry, University of Stuttgart, Pfaffenwaldring 55, 70569 Stuttgart

E-Mail: S.Bette@fkf.mpg.de

Additional Figures and Tables

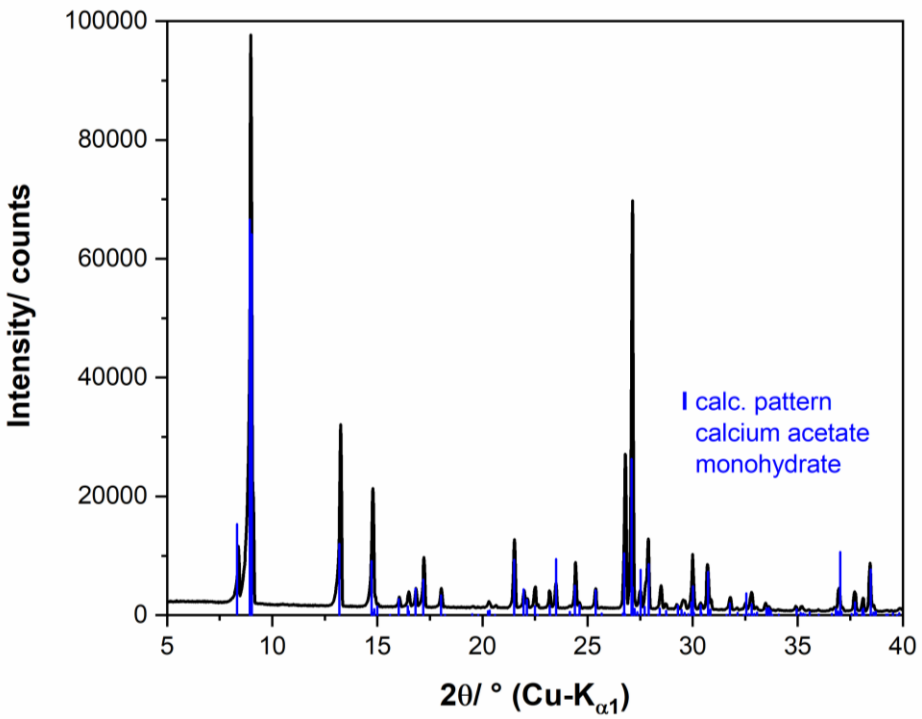

Figure S 1. Comparison of the measured diffraction pattern of crystallized $Ca(CH_3COO)_2 \cdot H_2O$ with peak positions and intensities that were calculated from its crystal structure.

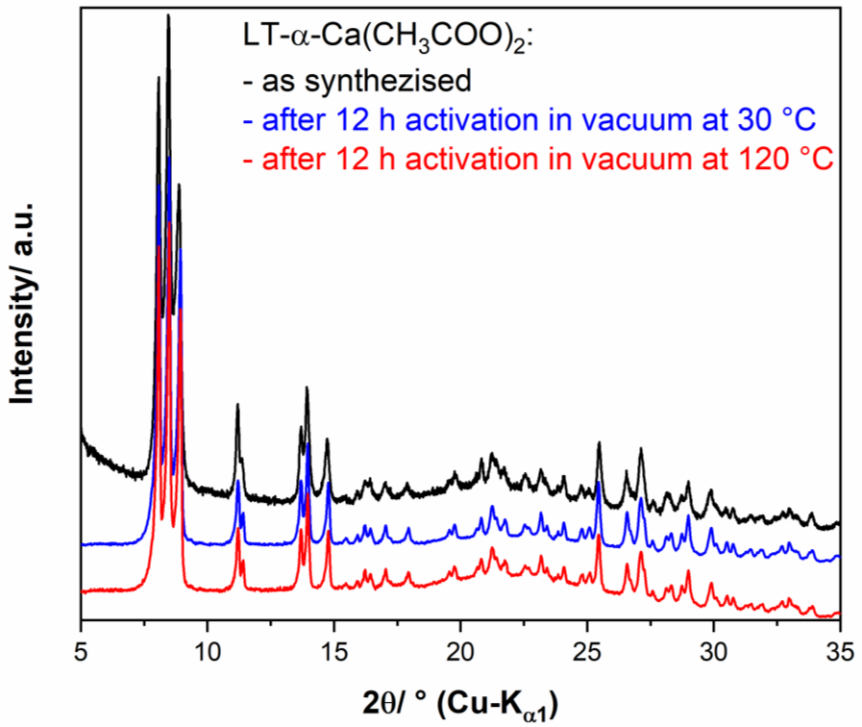

Figure S 2. XRPD patterns of LT-α-$Ca(CH_3COO_2$ at ambient conditions prior and after the adsorption and desorption measurements after activation in high vacuum.

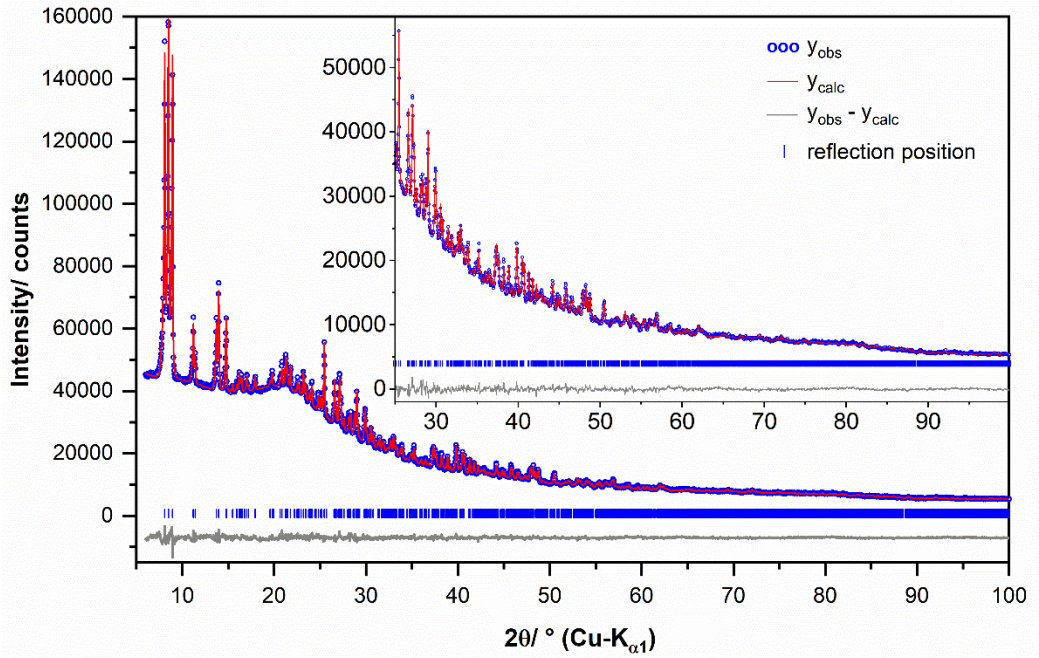

Figure S 3. Scattered X-ray intensities of LT-α-Ca(CH_3COO_2 at ambient conditions as a function of the diffraction angle 2θ. The observed pattern (circles) measured in Debye-Scherrer geometry, the best Rietveld fit profiles (line) the difference curve between the observed and the calculated profiles (below), and the calculated reflection positions (vertical ticks) are shown. The high angle part starting at 25° in 2θ is enlarged by a factor of 3 for clarity.

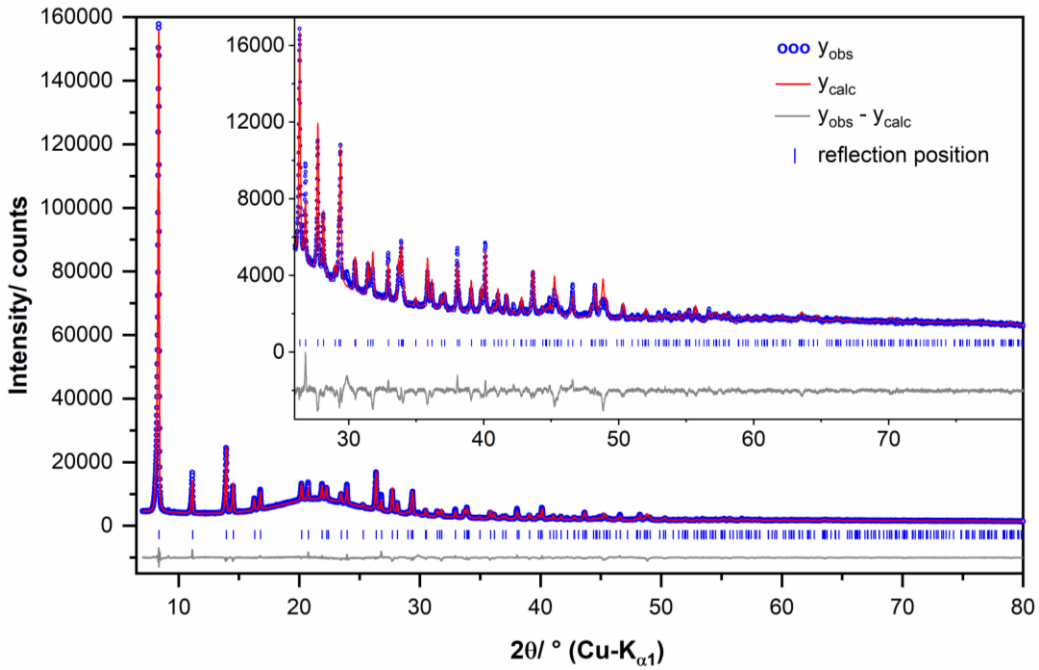

Figure S 4. Scattered X-ray intensities of HT-α-Ca(CH_3COO_2 at ambient conditions as a function of the diffraction angle 2θ. The observed pattern (circles) measured in Debye-Scherrer geometry, the best Rietveld fit profiles (line) the difference curve between the observed and the calculated profiles (below), and the calculated reflection positions (vertical ticks) are shown. The high angle part starting at 26° in 2θ is enlarged by a factor of 9 for clarity.

Table S 1. Crystallographic and Rietveld refinement data of LT- and HT-α-$Ca(CH_3COO)_2$.

substance name	LT-α- $Ca(CH_3COO)_2$	HT-α- $Ca(CH_3COO)_2$
molecular formula	$Ca(CH_3COO)_2$	$Ca(CH_3COO)_2$
sum formula	$C_4H_6CaO_4$	$C_4H_6CaO_4$
molecular weight (g/mol)	158.16	158.16
Temperature/ °C	298	573
space group	$P\bar{1}$ (2)	$R\bar{3}$ (148)
Z	6	18
a /Å	8.7168(3)	21.1030(5)
b /Å	12.6408(3)	21.1030(5)
c /Å	12.3084(3)	8.7965(2)
α /°	117.4363(17)	90
β /°	77.827(2)	90
γ /°	115.053(2)	120
V /Å³	1090.23(6)	3392.58(17)
ρ_{calc}/ g · cm^{-3}	1.45	1.39
Wavelength / Å	1.5406	1.5406
R-p /% *	1.28	3.07
R-*w*p /% *	1.60	4.05
R-*F*² /% *	0.63	2.57
starting angle (° 2θ)	6.0	7.0
final angle (° 2θ)	110.0	80.0
step width (° 2θ)	0.01	0.01
time/scan (h)	20	20
no. of variables	82	51

* *R*-p, *R*-*w*p, and *R*-*F*² as defined in TOPAS (Bruker AXS)

Table S 2. Fractional coordinates of LT- and HT-α-$Ca(CH_3COO)_2$.

Atom	Wyck.	Site	S.O.F.	*x/a*	*y/b*	*z/c*	B /Å²
LT-α-$Ca(CH_3COO)_2$, room temperature							
Ca1	2*i*	1	1	0.488(1)	0.5723(8)	0.6907(7)	1.4(2)[a]
Ca2	2*i*	1	1	0.0915(10)	0.2081(8)	0.1566(7)	1.4(2)[a]
Ca3	2*i*	1	1	0.8934(11)	0.3801(8)	0.0889(7)	1.4(2)[a]
C1a	2*i*	1	1	0.252(3)	0.535(2)	0.250(2)	1.2(2)[b]
C2a	2*i*	1	1	0.268(6)	0.662(3)	0.255(3)	1.2(2)[b]
O1a	2*i*	1	1	0.360(2)	0.523(2)	0.296(2)	1.2(2)[b]
O2a	2*i*	1	1	0.128(4)	0.436(3)	0.198(4)	1.2(2)[b]
C1b	2*i*	1	1	0.203(4)	0.405(3)	0.857(2)	1.2(2)[b]
C2b	2*i*	1	1	0.297(8)	0.331(4)	0.867(4)	1.2(2)[b]
O1b	2*i*	1	1	0.250(2)	0.462(2)	0.785(2)	1.2(2)[b]
O2b	2*i*	1	1	0.074(5)	0.410(4)	0.922(3)	1.2(2)[b]
C1c	2*i*	1	1	0.716(4)	0.256(4)	0.308(3)	1.2(2)[b]
C2c	2*i*	1	1	0.587(3)	0.215(2)	0.400(2)	1.2(2)[b]
O1c	2*i*	1	1	0.836(5)	0.213(6)	0.271(4)	1.2(2)[b]
O2c	2*i*	1	1	0.711(5)	0.328(5)	0.267(5)	1.2(2)[b]
C1d	2*i*	1	1	0.079(5)	0.922(3)	0.108(2)	1.2(2)[b]
C2d	2*i*	1	1	0.153(3)	0.923(2)	0.211(2)	1.2(2)[b]
O1d	2*i*	1	1	0.051(6)	1.017(4)	0.116(4)	1.2(2)[b]
O2d	2*i*	1	1	0.044(7)	0.822(4)	0.012(3)	1.2(2)[b]
C1e	2*i*	1	1	0.481(4)	0.217(3)	0.004(2)	1.2(2)[b]
C2e	2*i*	1	1	0.381(8)	0.089(3)	-0.097(3)	1.2(2)[b]
O1e	2*i*	1	1	0.398(2)	0.262(2)	0.102(1)	1.2(2)[b]
O2e	2*i*	1	1	0.635(5)	0.270(5)	-0.013(5)	1.2(2)[b]
C1f	2*i*	1	1	0.774(3)	0.680(3)	0.553(2)	1.2(2)[b]
C2f	2*i*	1	1	0.948(5)	0.724(6)	0.494(4)	1.2(2)[b]
O1f	2*i*	1	1	0.766(2)	0.728(2)	0.671(1)	1.2(2)[b]
O2r	2*i*	1	1	0.650(5)	0.601(4)	0.486(3)	1.2(2)[b]
HT-α-$Ca(CH_3COO)_2$, 300 °C							
Ca1	18*f*	1	1	0.7407(2)	0.0520(2)	0.6647(5)	3.0(3)[c]
C1a	18*f*	1	1	0.647(1)	0.568(1)	0.326(2)	3.0(3)[c]
C2a	18*f*	1	1	0.614(2)	0.490(1)	0.278(4)	3.0(3)[c]
O1a	18*f*	1	1	0.642(1)	0.616(1)	0.256(1)	3.0(3)[c]
O2a	18*f*	1	1	0.681(2)	0.578(2)	0.446(3)	3.0(3)[c]
C1b	18*f*	1	1	0.090(4)	0.846(4)	0.519(9)	3.0(3)[c]
C2b	18*f*	1	1	0.108(8)	0.899(5)	0.647(14)	3.0(3)[c]
O1b	18*f*	1	1	0.033(1)	0.788(1)	0.508(2)	3.0(3)[c]
O2b	18*f*	1	1	0.140(5)	0.870(7)	0.427(14)	3.0(3)[c]

[a]the B_{iso} values of all Ca-sites in LT-α-$Ca(CH_3COO)_2$ were constrained,
[b]the B_{iso} values of all acetate-related sites in LT-α-$Ca(CH_3COO)_2$ were constrained,
[c]all B_{iso} values were constrained to one global parameter.

Table S 3. Selected bond lengths and angles of LT- and HT-α-$Ca(CH_3COO)_2$.

Atoms	Distance/ Å	Atoms	Distance/ Å	Atoms	Distance/ Å
LT-α-$Ca(CH_3COO)_2$, room temperature					
Ca1-Ca1	4.17(1)				
Ca1-Ca2	3.89(1)	Ca2-Ca2	4.68(1)		
Ca1-Ca3	3.76(1)	Ca2-Ca3	3.72(2)	Ca3-Ca3	4.13(1)
Ca1-O1a	2.20(3)	Ca2-O2a	2.57(4)	Ca3-O2a	2.36(3)
Ca1-O1b	2.37(2)	Ca2-O1c	2.38(3)	Ca3-O1b	2.53(2)
Ca1-O2c	2.39(5)	Ca2-O1d	2.11(4)	Ca3-O2b	2.39(3)
Ca1-O1e	2.50(2)	Ca2-O2d	2.40(4)		2.60(5)
Ca1-O1f	2.44(2)	Ca2-O1e	2.49(2)	Ca3-O2c	2.59(4)
Ca1-O2f	2.34(2)	Ca2-O1f	2.32(2)	Ca3-O2d	2.51(4)
	2.71(5)			Ca3-O2e	2.35(5)
HT-α-$Ca(CH_3COO)_2$, 300 °C					
Ca(1)-Ca(1)	2x 3.793(6)	Ca(1)-O(1a)	2.42(1)	Ca(1)-O(1b)	2.41(1)
	4.448(5)		2.47(1)		2.56(2)
		Ca(1)-O(2a)	2.31(2)	Ca(1)-O(2b)	2.35(3)
					2.91(12)

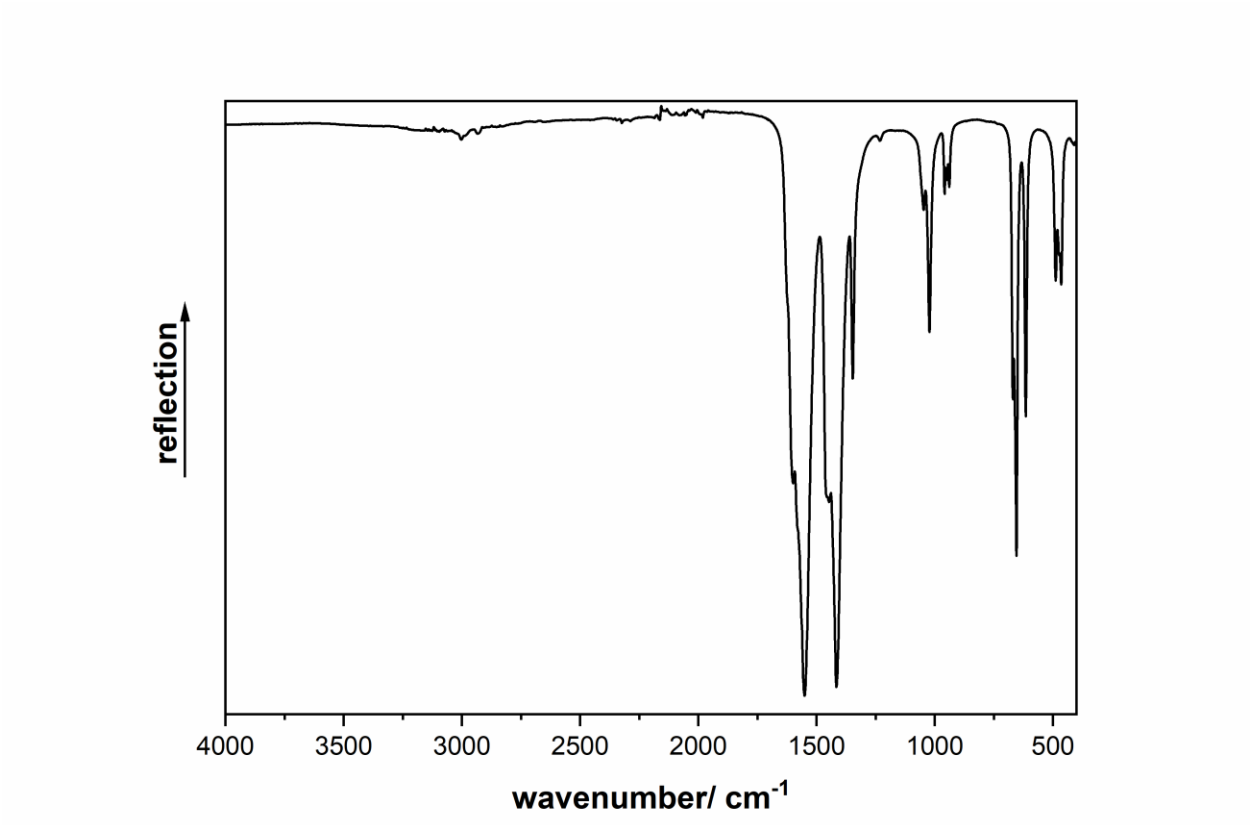

Figure S 5. IR-spectrum of LT-α-Ca(CH3COO)$_2$.

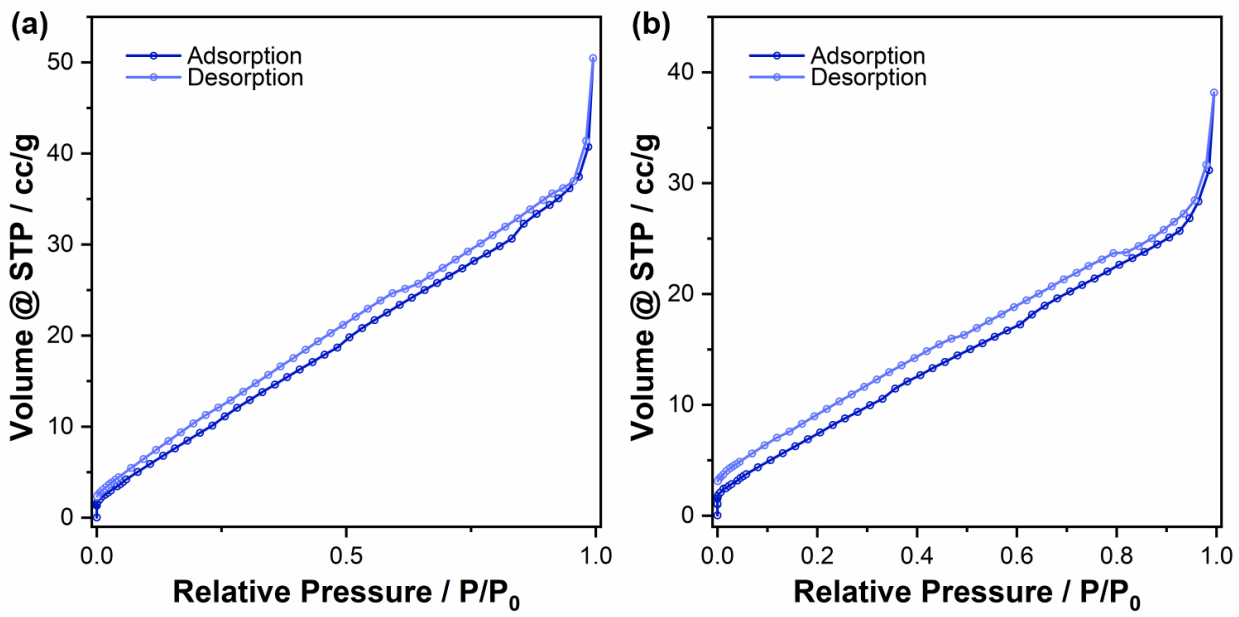

Figure S 6. N_2-adsorption and desorption curves of LT-α-$Ca(CH_3COO)_2$ after activating the samples under high vacuum at (a) room temperature and (b) at 120 °C for 12 h.

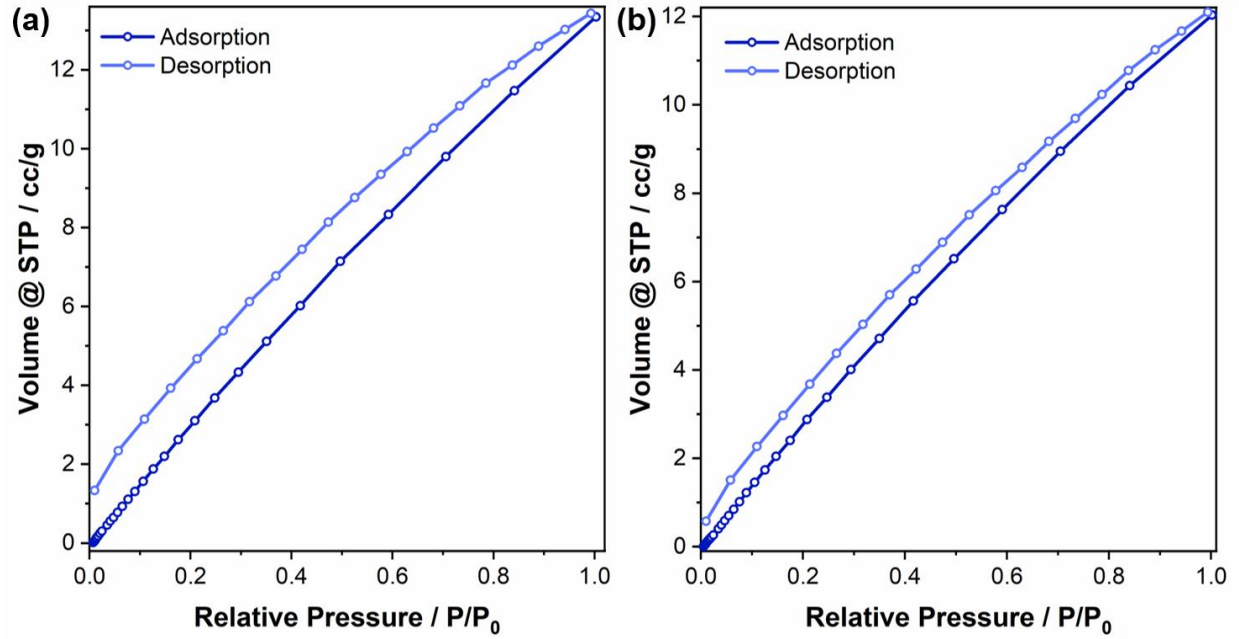

Figure S 7. CO_2-adsorption and desorption curves of LT-α-$Ca(CH_3COO)_2$ after activating the samples under high vacuum at (a) room temperature and (b) at 120 °C for 12 h.

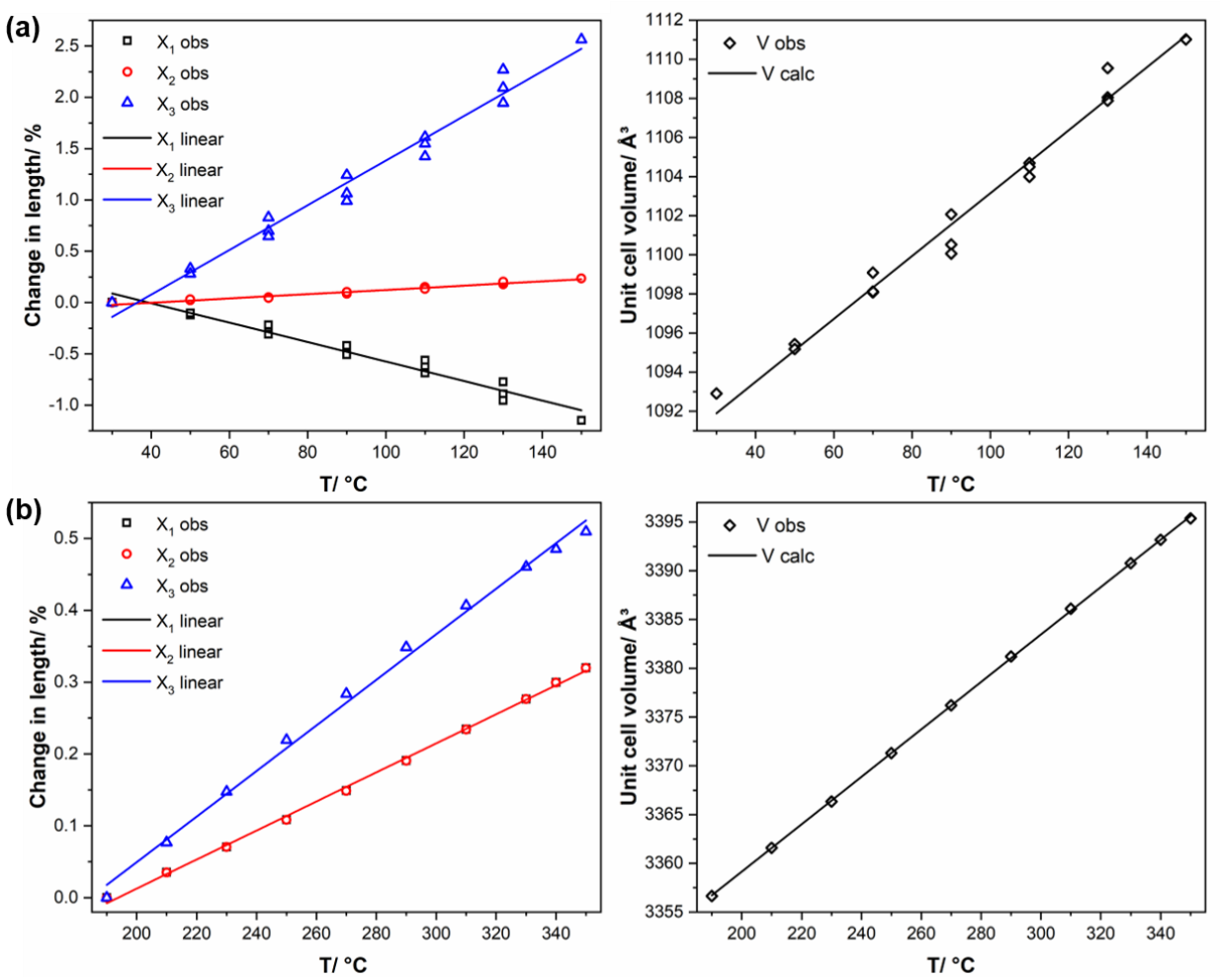

Figure S 8. Plots of the thermal expansion along the principal axes and of the overall volume expansion of LT-α-$Ca(CH_3COO)_2$ (a) and HT-α-$Ca(CH_3COO)_2$ (b).