Cascade of High-Pressure Transitions of Claudetite II and the First Polar Phase of Arsenic(III) Oxide

Supporting Information

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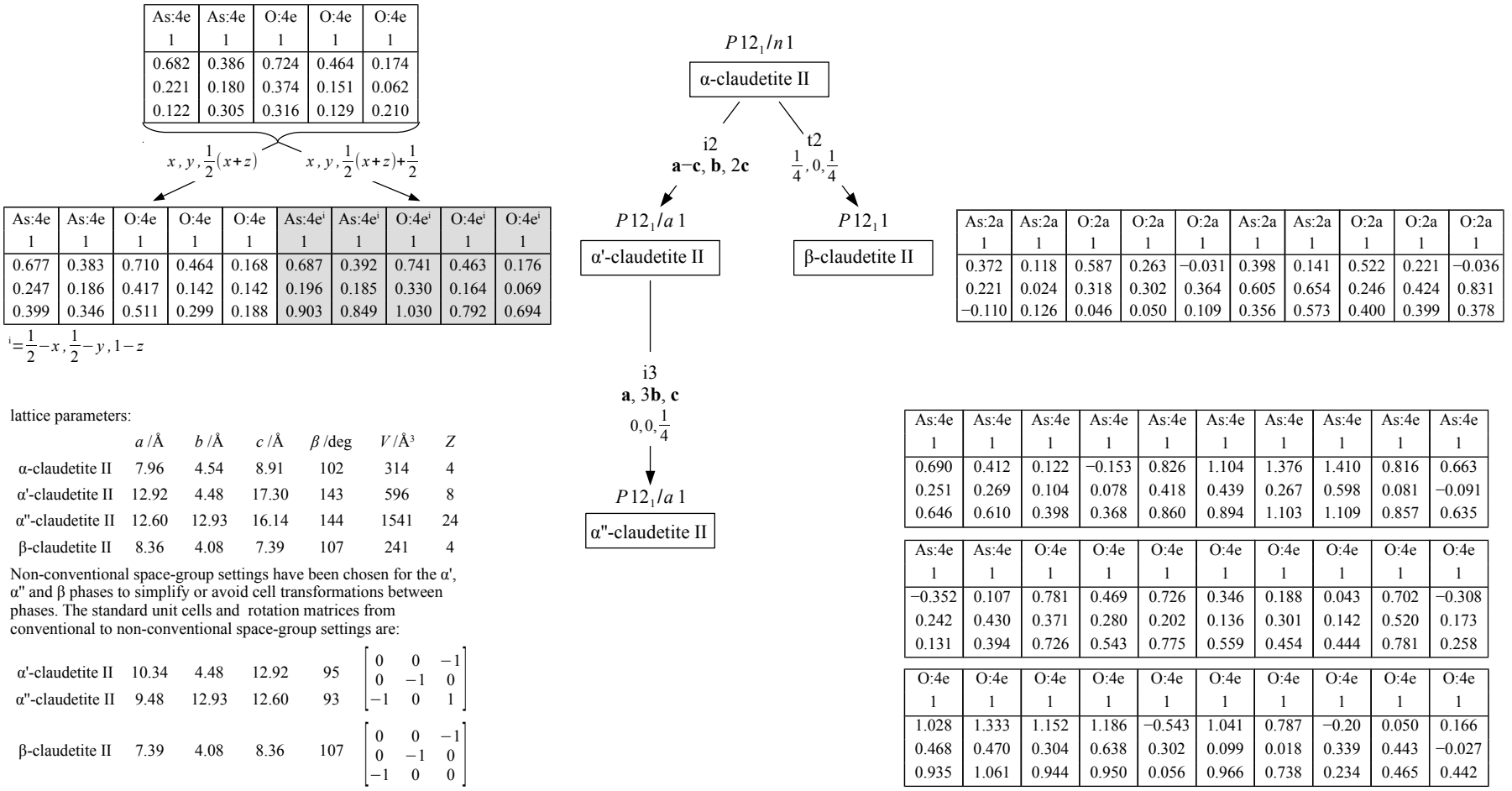
Table S1: Structural parameters for experimentally determined crystal structure of claudetite II at various pressures.

Phase	p /GPa	a /Å	b /Å	c /Å	β /deg	V /Å^3	Z	R_{int}	Reflections measured/ independent/ observed	Restraints	$\Delta\rho_{\mathrm{min}}/\Delta\rho_{\mathrm{max}}$	R_1
α	1.00(1)E-04	8.0256(3)	4.57553(11)	9.142(2)	101.666(11)	328.79(9)	4	0.0439	940/483/439	0	−1.03/+0.98	0.0392
α	0.37(5)	7.9853(4)	4.55112(13)	9.000(3)	102.014(13)	319.93(11)	4	0.0288	857/440/406	0	−0.58/+0.66	0.0327
α	0.74(5)	7.9615(4)	4.53586(14)	8.911(3)	102.155(14)	314.59(11)	4	0.0464	878/426/399	0	−0.72/+0.66	0.0338
α	1.42(5)	7.9216(2)	4.50673(7)	8.7646(14)	102.548(7)	305.42(5)	4	0.0331	824/423/389	0	−1.11/+1.02	0.0431
α’	2.08(11)	12.9231(8)	4.48160(10)	17.2952(15)	143.480(4)	596.10(7)	8	0.0486	1606/816/652	0	−1.60/+1.17	0.0481
α’	2.59(5)	12.8439(14)	4.46320(10)	17.122(3)	143.381(8)	585.47(14)	8	0.0318	1167/735/638	0	−1.81/+2.29	0.0646
α’	3.23(10)	12.792(3)	4.4390(3)	17.001(5)	143.454(15)	574.9(3)	8	0.3387	1128/914/253	-	-	fail[a]
α’	3.75(5)	12.7203(7)	4.42690(10)	16.8699(13)	143.284(4)	567.94(6)	8	0.0384	1648/784/672	0	−1.36/+2.05	0.0452
α’	4.5(4)	12.6524(7)	4.40820(10)	16.7237(14)	143.209(4)	558.62(7)	8	0.0496	1614/776/671	0	−1.30/+2.37	0.0524
α’	5.14(7)	12.5859(5)	4.3845(5)	16.5934(9)	143.183(3)	548.73(7)	8	0.0467	1594/753/664	0	−1.22/+2.45	0.0488
α”	6.08(5)	12.727(10)	13.0569(7)	16.455(17)	143.8(2)	1614(5)	24	0.0356	3230/1866/677	633	−2.25/+3.42	0.1166
α”	7.23(15)	12.655(10)	12.9892(7)	16.282(18)	143.9(2)	1576(5)	24	0.0381	3110/1792/598	633	−2.38/+3.74	0.1308
α”	8.51(11)	12.599(11)	12.9232(7)	16.142(18)	144.1(2)	1541(5)	24	0.0364	3127/1758/628	633	−2.96/+4.76	0.1488
α”	9.60(7)	12.543(10)	12.8595(7)	16.032(18)	144.2(2)	1512(5)	24	0.0407	3094/1739/597	633	−2.79/+5.45	0.1702
β	11.68(7)	8.3570(10)	4.0889(2)	7.400(4)	106.90(3)	241.94(14)	4	0.1105	738/573/384	67	−1.74/+2.10	0.1179
β	11.95(5)	8.3494(10)	4.0797(2)	7.388(5)	106.91(3)	240.78(17)	4	0.0993	726/562/449	67	−2.28/+2.56	0.1068
β	11.92(5)	8.3557(17)	4.0829(3)	7.385(7)	107.04(5)	240.9(2)	4	0.0712	701/542/522	67	−1.45/+1.49	0.0742
β	14.44(5)	8.3192(9)	4.0286(2)	7.298(3)	106.84(3)	234.10(11)	4	0.0959	682/532/484	67	−1.80/+1.74	0.0867
β	21.16(11)	8.2230(7)	3.9071(2)	7.130(3)	106.53(2)	219.61(10)	4	0.0907	637/499/447	67	−1.82/+2.23	0.0929
β	9.54(11)	8.3873(8)	4.1360(2)	7.490(4)	107.03(3)	248.43(14)	4	0.0427	681/551/495	67	−1.36/+1.50	0.0694
β	7.4(4)	8.4114(5)	4.18950(10)	7.614(3)	107.025(19)	256.56(11)	4	0.0424	700/560/504	67	−1.37/+1.44	0.0833
α’	4.85(10)	12.588(3)	4.3812(2)	16.593(4)	143.199(13)	548.2(2)	8	0.0693	1471/700/536	66	−3.34/+3.86	0.1208
α’	2.31(18)	12.905(3)	4.4711(3)	17.262(6)	143.483(19)	592.7(3)	8	0.0498	1632/793/604	66	−2.53/+3.09	0.1066
α	1.30(5)	7.9307(6)	4.5105(2)	8.784(5)	102.53(2)	306.72(16)	4	0.0438	789/383/319	0	−1.43/+1.32	0.0850
α	1.00(1)E−04	8.0290(6)	4.57732(16)	9.141(5)	101.65(2)	329.00(18)	4	0.0389	845/448/399	0	−1.78/+2.56	0.1051

[a] due to poor experimental setup centering



lattice parameters:

	a /Å	b /Å	c /Å	β /deg	V /Å^3	Z
α-claudetite II	7.96	4.54	8.91	102	314	4
α'-claudetite II	12.92	4.48	17.30	143	596	8
α''-claudetite II	12.60	12.93	16.14	144	1541	24
β-claudetite II	8.36	4.08	7.39	107	241	4

Non-conventional space-group settings have been chosen for the α', α'' and β phases to simplify or avoid cell transformations between phases. The standard unit cells and rotation matrices from conventional to non-conventional space-group settings are:

α'-claudetite II	10.34	4.48	12.92	95	$\begin{bmatrix} 0 & 0 & -1 \\ 0 & -1 & 0 \\ -1 & 0 & 1 \end{bmatrix}$
α''-claudetite II	9.48	12.93	12.60	93	
β-claudetite II	7.39	4.08	8.36	107	$\begin{bmatrix} 0 & 0 & -1 \\ 0 & -1 & 0 \\ -1 & 0 & 0 \end{bmatrix}$

Figure S1: Bärnighausen tree for the family of claudetite II ambient pressure and high-pressure polymorphic forms.

Table S2: The relationships between the reduced (pseudo)translation vectors and the unit cell vectors. The reduced vectors coincide with crystallographic translational symmetry vectors for the α and β phases, whereas for the α' and α" phases they represent only pseudo-translational symmetry.

α	α'	α"	β
$\overrightarrow{a}_{\mathrm{red}} = \overrightarrow{a}_{\alpha}$	$\overrightarrow{a}_{\mathrm{red}} = \overrightarrow{a}_{\alpha'} + \frac{1}{2}\overrightarrow{c}_{\alpha'}$	$\overrightarrow{a}_{\mathrm{red}} = \overrightarrow{a}_{\alpha"} + \frac{1}{2}\overrightarrow{c}_{\alpha"}$	$\overrightarrow{a}_{\mathrm{red}} = \overrightarrow{a}_{\beta}$
$\overrightarrow{b}_{\mathrm{red}} = \overrightarrow{b}_{\alpha}$	$\overrightarrow{b}_{\mathrm{red}} = \overrightarrow{b}_{\alpha'}$	$\overrightarrow{b}_{\mathrm{red}} = \frac{1}{3}\overrightarrow{b}_{\alpha"}$	$\overrightarrow{b}_{\mathrm{red}} = \overrightarrow{b}_{\beta}$
$\overrightarrow{c}_{\mathrm{red}} = \overrightarrow{c}_{\alpha}$	$\overrightarrow{c}_{\mathrm{red}} = \frac{1}{2}\overrightarrow{c}_{\alpha'}$	$\overrightarrow{c}_{\mathrm{red}} = \frac{1}{2}\overrightarrow{c}_{\alpha"}$	$\overrightarrow{c}_{\mathrm{red}} = \overrightarrow{c}_{\beta}$

Table S3: The reduced lattice parameters at various pressures.

phase	p /GPa	a_{red} /Å	b_{red} /Å	c_{red} /Å	β_{red}/deg
α	1.00(1)E−04	8.0256	4.5755	9.1420	101.67
α	0.37(5)	7.9853	4.5511	9.0000	102.01
α	0.74(5)	7.9615	4.5359	8.9110	102.16
α	1.42(5)	7.9216	4.5067	8.7646	102.55
α'	2.08(11)	7.8845	4.4816	8.6476	102.73
α'	2.59(5)	7.8581	4.4632	8.5610	102.85
α'	3.23(10)	7.8216	4.4390	8.5005	103.11
α'	3.75(5)	7.8062	4.4269	8.4350	103.04
α'	4.5(4)	7.7816	4.4082	8.3619	103.15
α'	5.14(7)	7.7492	4.3845	8.2967	103.27
α"	6.08(5)	7.7892	4.3523	8.2275	105.33
α"	7.23(15)	7.7421	4.3297	8.1410	105.74
α"	8.51(11)	7.6899	4.3077	8.0710	106.13
α"	9.60(7)	7.6477	4.2865	8.0160	106.47
β	11.68(7)	8.3570	4.0889	7.4000	106.90
β	11.95(5)	8.3494	4.0797	7.3880	106.91
β	11.92(5)	8.3557	4.0829	7.3850	107.04
β	14.44(5)	8.3192	4.0286	7.2980	106.84
β	21.16(11)	8.2230	3.9071	7.1300	106.53
β	9.54(11)	8.3873	4.1360	7.4900	107.03
β	7.4(4)	8.4114	4.1895	7.6140	107.03
α'	4.85(10)	7.7486	4.3812	8.2965	103.30
α'	2.31(18)	7.8740	4.4711	8.6310	102.76
α	1.30(5)	7.9307	4.5105	8.7830	102.53
α	1.00(1)E−04	8.0290	4.5773	9.1410	101.65

Table S4: Linear moduli for the a_{red}, b_{red} and c_{red} directions obtained with a linearized 2$^{\mathrm{nd}}$ order Birch-Murnaghan EoS. One set of parameters was used for the α, α' and α" phases and another one for the β phase.

phase	$M(a_{\mathrm{red}})$ /GPa	$M(b_{\mathrm{red}})$ /GPa	$M(c_{\mathrm{red}})$ /GPa
α	116(4)	90(5)	28.7(7)
β	410(40)	56(9)	74(7)

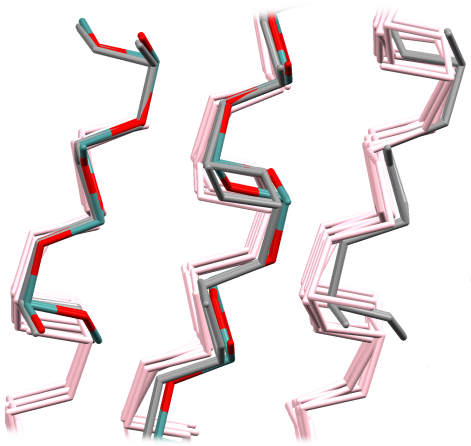


Figure S2: Overlay of the α, α' and α" forms of claudetite II crystal structures viewed along Y axis. The arsenic and oxygen atoms in the α form are colored green and red, respectively, while the α' and α" are colored grey and pink, respectively. The overlay picture was created using Mercury.[1,2]

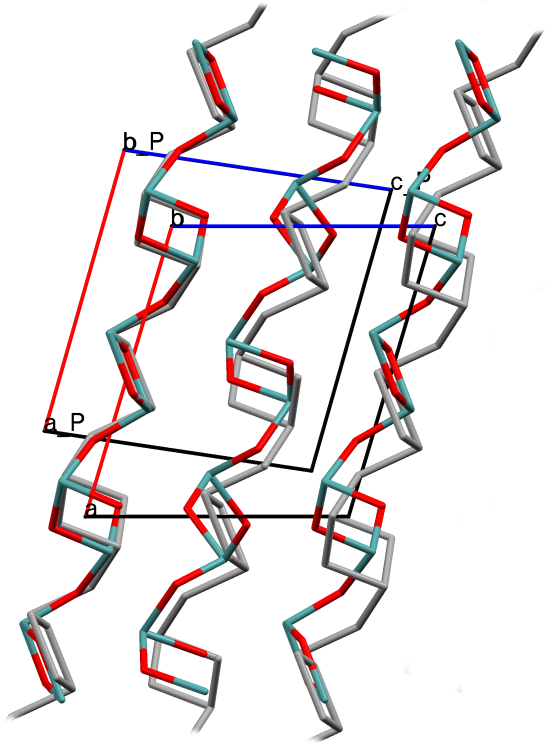


Figure S3: Overlay of the claudetite II crystal structure predicted under 19.6 GPa[3], colored dark grey, with the crystal structure of polymorph β determined experimentally at 21.16(11) GPa, with arsenic and oxygen atom colored green and red, respectively. The overlay picture was created using Mercury.[1,2]

References

(1) Macrae, C. F.; Edgington, P. R.; McCabe, P.; Pidcock, E.; Shields, G. P.; Taylor, R.; Towler, M.; van de Streek, J. *J. Appl. Crystallogr.* **2006**, *39*, 453–457.

(2) Macrae, C. F.; Bruno, I. J.; Chisholm, J. A.; Edgington, P. R.; McCabe, P.; Pidcock, E.; Rodriguez-Monge, L.; Taylor, R.; van de Streek, J.; Wood, P. A. *J. Appl. Crystallogr.* **2008**, *41*, 466–470.

(3) Guńka, P. A.; Dranka, M.; Piechota, J.; Żukowska, G. Z.; Zalewska, A.; Zachara, J. *Cryst. Growth Des.* **2012**, *12*, 5663–5670.