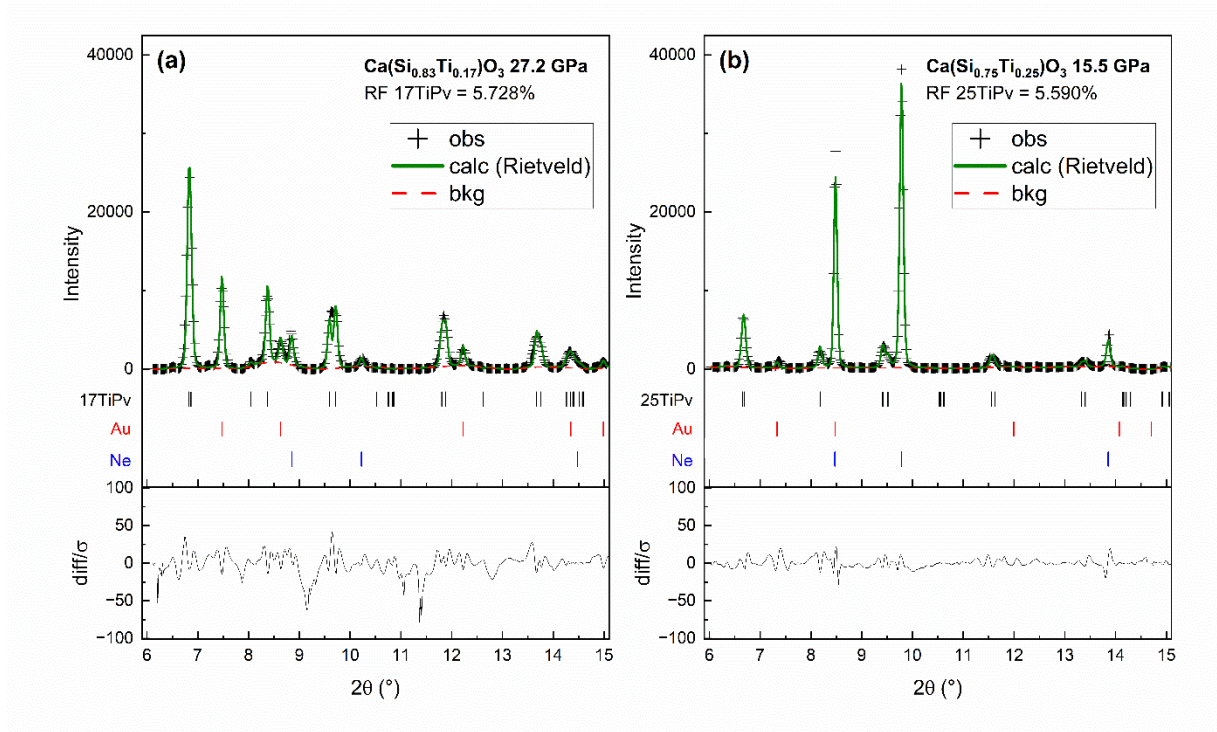
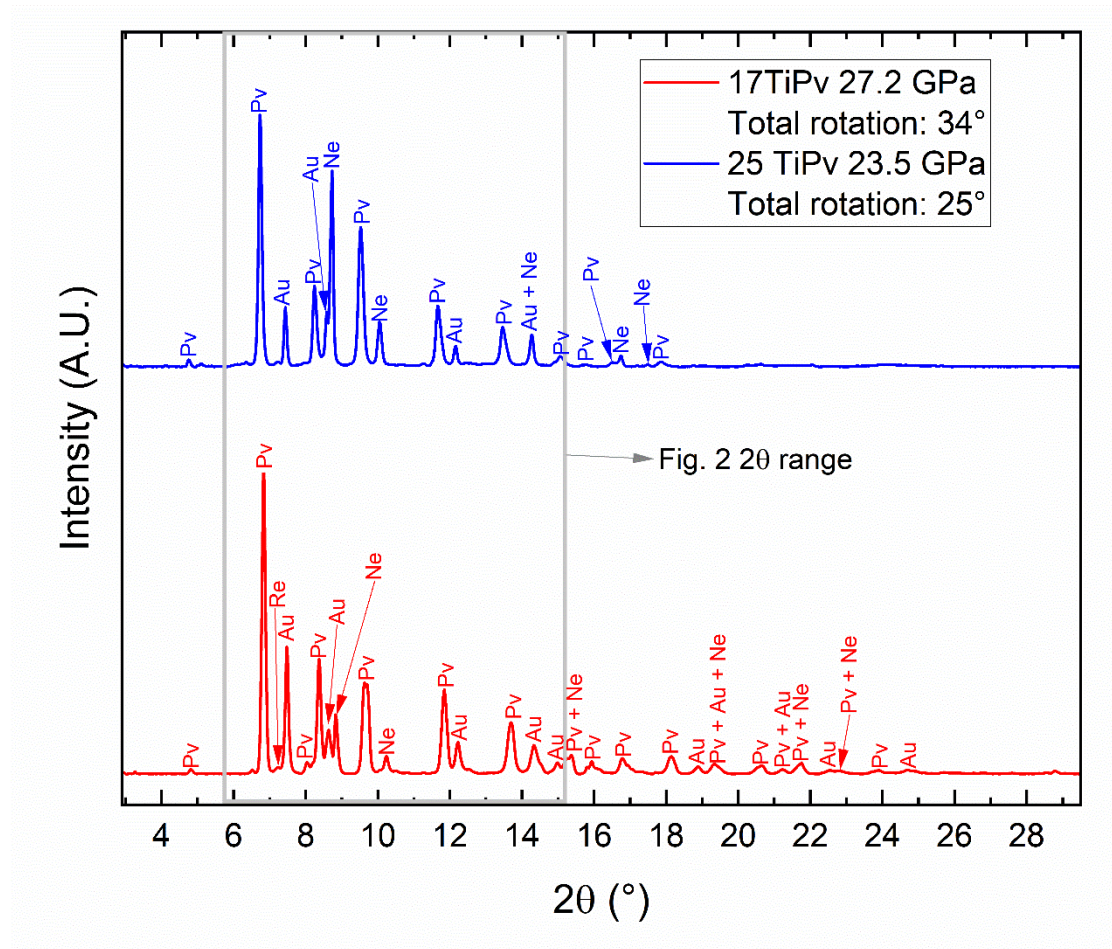


## Supplemental Materials



*Figure S1.* Fitting of X-ray diffraction patterns of (a) 17TiPv and (b) 25TiPv after heating (same spectrum as Fig. 2a and Fig. 2c, respectively) by GSAS-II. The RF values of two perovskite phases are all within 10%.



*Figure S2.* Representative full-range XRD patterns of 17TiPv and 25TiPv. Peaks with  $2\theta > 15^\circ$  are relatively weak in the experiment of 17TiPv, and the peaks with  $2\theta > 15^\circ$  in the experiment of 25TiPv are even weaker. In Fig.2, we plot where the peaks are strong and representative for structure determination.

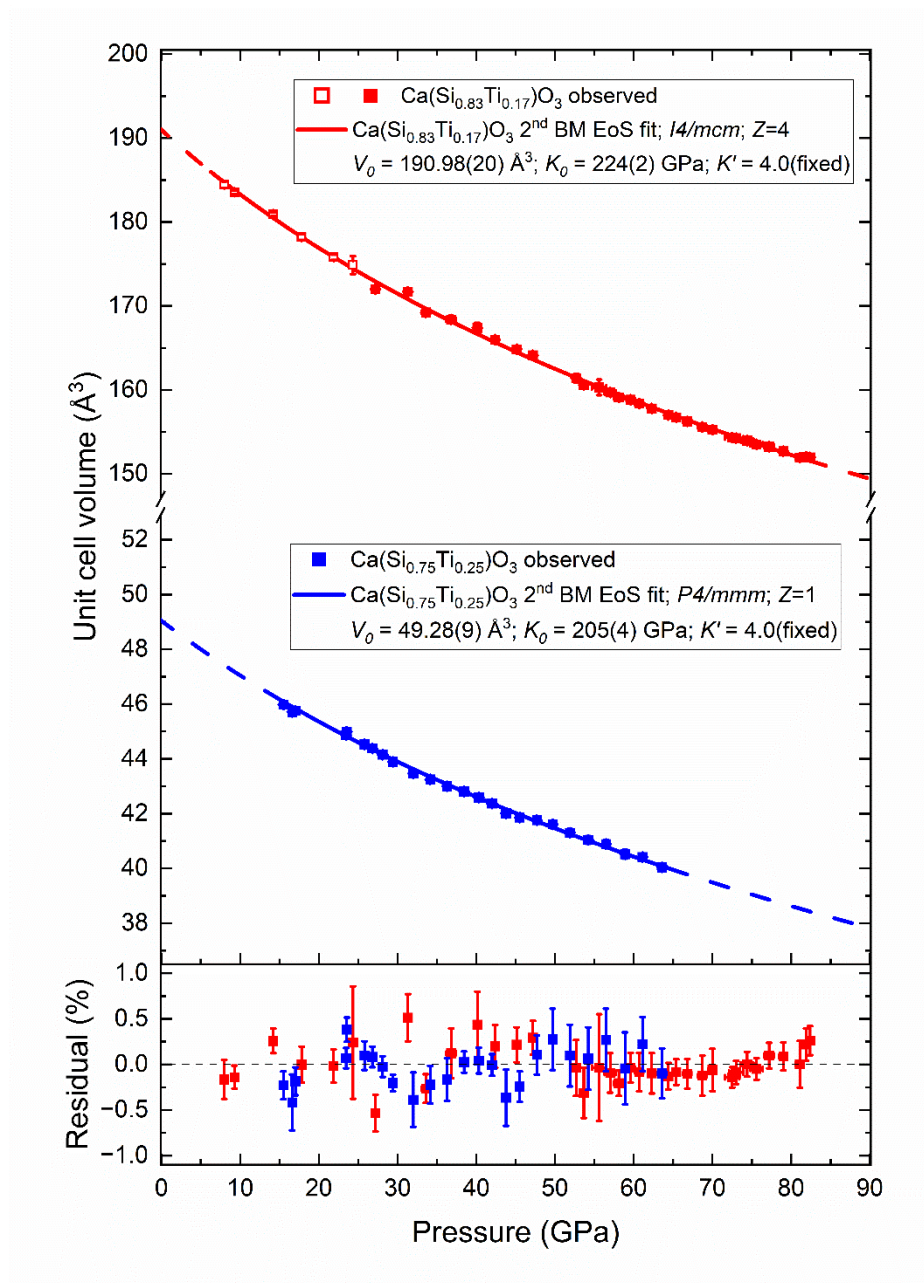


Figure S3. 2<sup>nd</sup>-order Birch-Murnaghan equation of state fitting of unit cell volume of 17TiPv and 25TiPv. Residuals are generally within 0.5%.



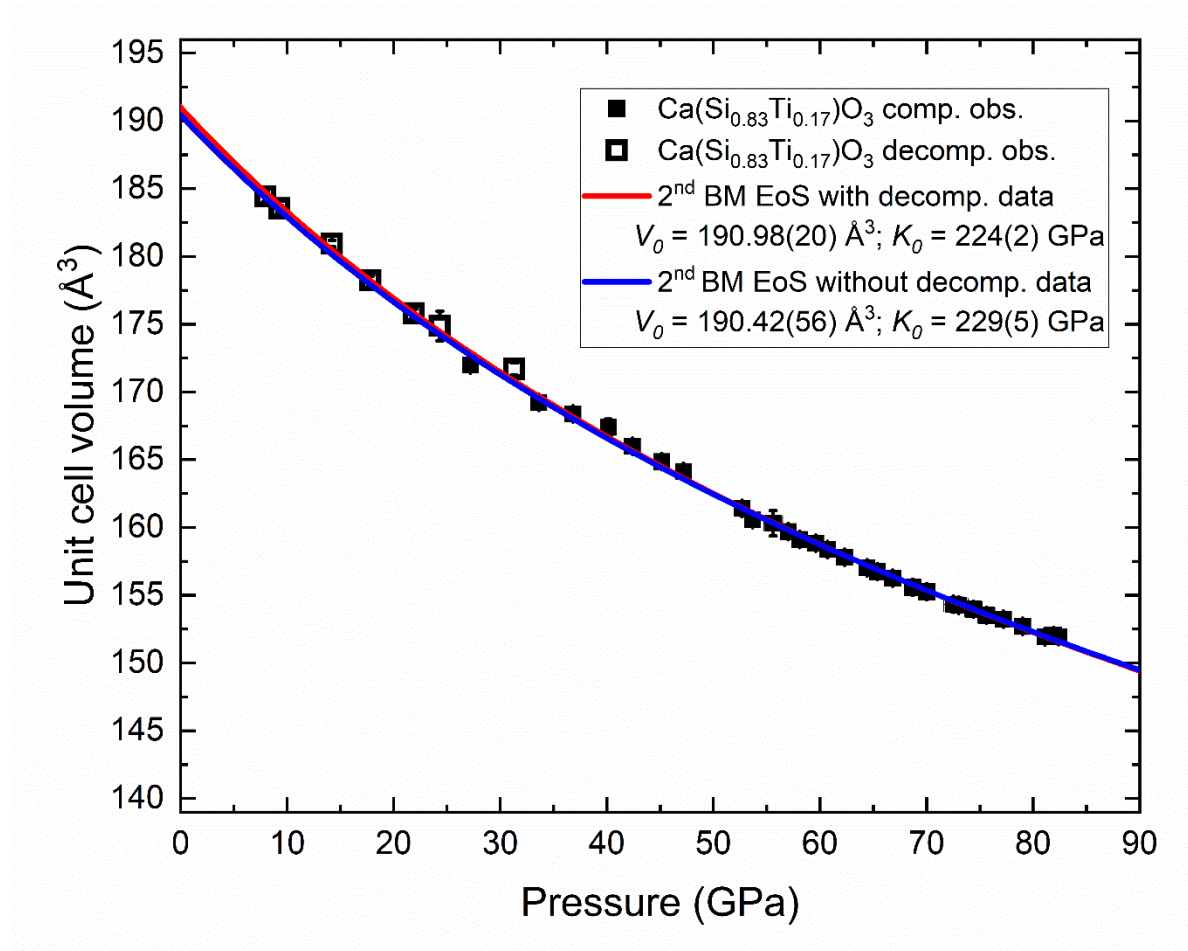


Figure S4. 2<sup>nd</sup>-order Birch-Murnaghan equation of state of 17TiPv with (red) and without (blue) considering decompression data. The fitted  $V_0$  with and without considering decompression data are  $190.98 (\pm 0.20) \text{ \AA}^3$  and  $190.42 (\pm 0.56) \text{ \AA}^3$ , respectively. The fitted  $K_0$  with and without considering decompression data are  $224 (\pm 2) \text{ GPa}$  and  $229 (\pm 5) \text{ GPa}$ , respectively. Therefore, excluding the decompression data has a minor effect on the equation of state of 17TiPv.

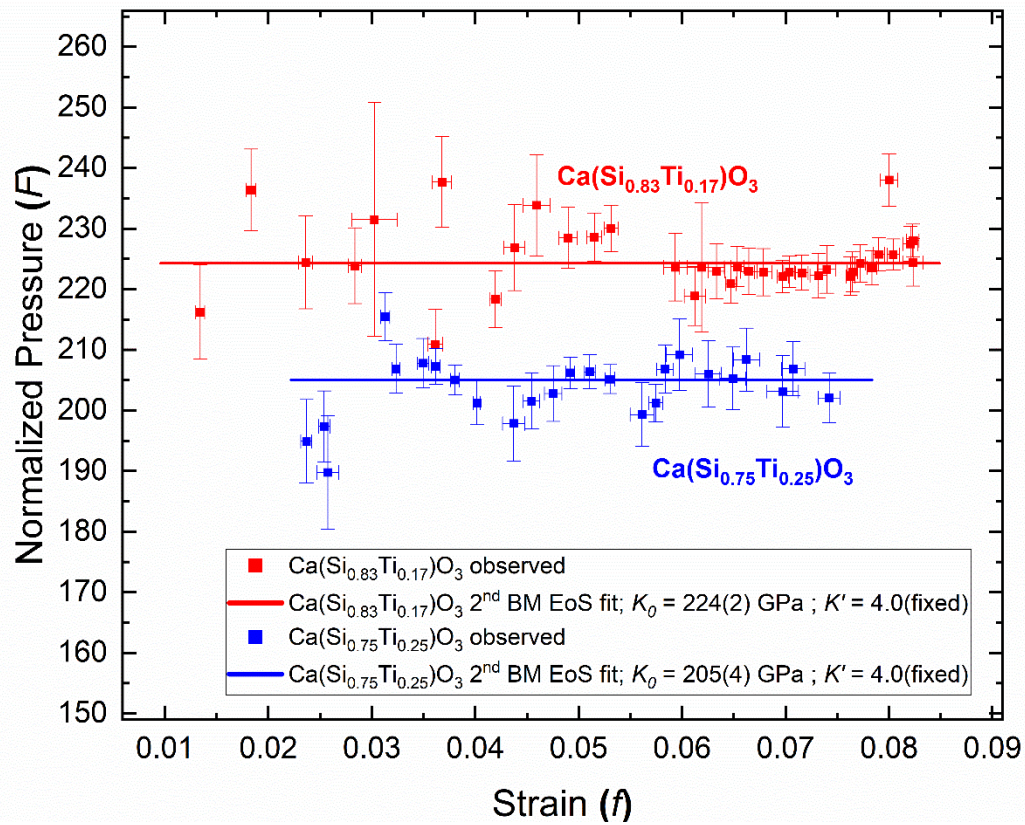


Figure S5. Eulerian strain-normalized pressure ( $f$ - $F$ ) plot of the data based on the Birch-Murnaghan equation of state of 17TiPv (red) and 25TiPv (blue). Both phases show  $K'$  close to 4.0.

TABLE S1. EPMA result of the starting material of 17TiPv glass.

Probe spot	CaO wt%	SiO <sub>2</sub> wt%	TiO <sub>2</sub> wt%	Total
Spot 1	48.48(8)	40.43(6)	10.63(8)	99.54
Spot 2	48.47(8)	40.46(6)	10.80(8)	99.73
Spot 3	48.61(8)	40.36(6)	10.90(8)	99.87
Spot 4	48.61(8)	40.49(6)	10.86(8)	99.95
Spot 5	48.56(8)	40.43(6)	10.61(8)	99.60
Spot 6	48.61(8)	40.22(6)	10.61(8)	99.45
Spot 7	48.41(8)	40.24(6)	10.79(8)	99.43
Spot 8	48.42(8)	40.01(6)	10.95(8)	99.38
Spot 9	48.59(8)	40.20(6)	10.81(8)	99.60
Spot 10	48.38(8)	40.09(6)	10.95(8)	99.42
Spot 11	48.02(8)	39.33(6)	10.83(8)	98.18
Spot 12	48.21(8)	39.49(6)	10.88(8)	98.58
Spot 13	48.44(8)	39.75(6)	10.67(8)	98.86
Spot 14	48.52(8)	40.24(6)	10.58(8)	99.34
Spot 15	48.70(8)	40.21(6)	10.94(8)	99.85
Spot 16	48.47(8)	40.19(6)	10.78(8)	99.44
Spot 17	48.43(8)	40.10(6)	10.76(8)	99.29
Spot 18	48.30(8)	39.96(6)	10.69(8)	98.95
Spot 19	48.31(8)	40.11(6)	10.75(8)	99.17
Spot 20	48.55(8)	39.71(6)	10.89(8)	99.15
Spot 21	48.73(8)	40.40(6)	10.74(8)	99.87
Spot 22	48.59(8)	40.01(6)	10.74(8)	99.34
Spot 23	48.66(8)	40.56(6)	10.63(8)	99.85
Spot 24	48.58(8)	40.49(6)	10.76(8)	99.83
Spot 25	48.80(8)	40.48(6)	10.87(8)	100.15
Spot 26	48.67(8)	40.29(6)	10.71(8)	99.67
Spot 27	48.71(8)	40.54(6)	10.84(8)	100.08
Spot 28	48.85(8)	40.57(6)	10.84(8)	100.26
Spot 29	48.75(8)	40.68(6)	11.02(8)	100.44
Spot 30	48.33(8)	39.16(6)	10.94(8)	98.43
Spot 31	48.33(8)	39.25(6)	10.96(8)	98.54
Spot 32	47.56(8)	40.40(6)	10.73(8)	98.69
Spot 33	48.49(8)	39.36(6)	10.70(8)	98.55
Spot 34	48.41(8)	39.58(6)	10.62(8)	98.61
Average	48.29(8)	40.11(6)	10.79(8)	99.39

*Note:* The numbers in the parentheses are the uncertainties calculated from analytical errors in relative percentage for the last digit (typically 0.17%, 0.16%, and 0.72% for CaO, SiO<sub>2</sub>, and TiO<sub>2</sub>, respectively). The average chemical formula of 17TiPv glass is Ca<sub>1.08</sub>Si<sub>0.83</sub>Ti<sub>0.17</sub>O<sub>3.08</sub> according to the average amount of each oxide.

TABLE S2. EPMA result of the starting material of 25TiPv glass.

Probe spot	CaO wt%	SiO <sub>2</sub> wt%	TiO <sub>2</sub> wt%	Total
Spot 1	46.69(8)	37.34(6)	15.95(9)	99.98
Spot2	46.88(8)	37.49(6)	15.59(9)	99.97
Spot3	46.52(8)	37.33(6)	16.09(9)	99.95
Spot4	46.40(8)	36.53(6)	16.99(9)	99.92
Spot5	46.70(8)	37.37(6)	15.88(9)	99.94
Spot6	46.89(8)	36.60(6)	16.44(9)	99.93
Spot7	46.76(8)	36.48(6)	16.72(9)	99.96
Spot8	46.97(8)	36.67(6)	16.29(9)	99.93
Spot9	46.38(8)	36.57(6)	17.02(9)	99.98
Spot10	46.52(8)	37.19(6)	16.25(9)	99.96
Spot11	46.83(8)	36.83(6)	16.32(9)	99.98
Spot12	46.81(8)	37.16(6)	15.99(9)	99.96
Spot13	46.58(8)	37.23(6)	16.14(9)	99.94
Spot14	46.73(8)	36.66(6)	16.54(9)	99.93
Spot15	46.67(8)	36.91(6)	16.37(9)	99.95
Spot16	46.59(8)	36.82(6)	16.52(9)	99.93
Average	46.68(8)	36.95(6)	16.32(9)	99.95

*Note:* The numbers in the parentheses are the uncertainties calculated from analytical errors in relative percentage for the last digit (typically 0.16%, 0.17%, and 0.56% for CaO, SiO<sub>2</sub>, and TiO<sub>2</sub>, respectively). The average chemical formula of 25TiPv glass is Ca<sub>1.02</sub>Si<sub>0.75</sub>Ti<sub>0.25</sub>O<sub>3.02</sub>, according to the quantity of each oxide.

TABLE S3. Representative peaks with their  $2\theta$  and corresponding  $d$ -space of 17TiPv ( $I4/mcm$ ) at 27.2 GPa.

$hkl$	$2\theta$ cal. (°)	$2\theta$ obs. (°)	$d$ cal. (Å)	$d$ obs. (Å)	$\Delta 2\theta$ (°) (obs.-cal.)	$\Delta d$ (Å) (obs.-cal.)
112	6.8217	6.8287	2.4809	2.4783	0.007	-0.0026
200	6.8521	6.8374	2.4699	2.4752	-0.023	0.0053
211	8.0301	8.0242	2.1080	2.1096	-0.006	0.0016
202	8.3697	8.3729	2.0226	2.0218	0.003	-0.0008
004	9.6097	9.6229	1.7621	1.7597	0.013	-0.0024
220	9.6961	9.7300	1.7465	1.7404	0.034	-0.0061
213	10.5239	10.4985	1.6094	1.6133	-0.025	0.0039
204	11.8118	11.8223	1.4345	1.4332	0.010	-0.0013
312	11.8648	11.8907	1.4281	1.4250	0.026	-0.0031
224	13.6677	13.6450	1.2404	1.2425	-0.023	0.0021
400	13.7288	13.7325	1.2349	1.2346	0.004	-0.0003
411	14.3575	14.3376	1.1811	1.1828	-0.020	0.0017

*Note:*  $\Delta 2\theta$  and  $\Delta d$  are the difference between the observed value and the calculated value of  $2\theta$  and  $d$ -spacing, respectively.



TABLE S4. Representative peaks with their  $2\theta$  and corresponding  $d$ -space of 25TiPv ( $P4/mmm$ ) at 23.5 GPa.

$hkl$	$2\theta$ cal. ( $^{\circ}$ )	$2\theta$ obs. ( $^{\circ}$ )	$d$ cal. ( $\text{\AA}$ )	$d$ obs. ( $\text{\AA}$ )	$\Delta 2\theta$ ( $^{\circ}$ ) (obs.-cal.)	$\Delta d$ ( $\text{\AA}$ ) (obs.-cal.)
110	6.6555	6.6571	2.5428	2.5421	0.0017	-0.0006
101	6.6935	6.6851	2.5283	2.5315	-0.0084	0.0032
111	8.1846	8.1781	2.0683	2.0699	-0.0066	0.0017
200	9.4175	9.4240	1.7980	1.7968	0.0064	-0.0012
002	9.5250	9.5126	1.7778	1.7801	-0.0124	0.0023
211	11.5627	11.5471	1.4653	1.4672	-0.0156	0.0020
112	11.6286	11.6325	1.4570	1.4565	0.0038	-0.0005
220	13.3335	13.3309	1.2714	1.2716	-0.0026	0.0002
202	13.4099	13.4342	1.2642	1.2619	0.0243	-0.0023

*Note:*  $\Delta 2\theta$  and  $\Delta d$  are the difference between the observed value and the calculated value of  $2\theta$  and  $d$ -spacing, respectively.

TABLE S5 Lattice parameters and unit cell volume of 17TiPv under high pressure.

$P$ (GPa)	$a$ (Å)	$c$ (Å)	$V$ (Å <sup>3</sup> )
8.0(1)	5.063(4)	7.196(9)	184.43(39)
9.3(1)	5.052(3)	7.192(6)	183.54(23)
14.2(1)	5.030(3)	7.151(6)	180.94(24)
17.8(2)	5.005(4)	7.114(9)	178.21(35)
21.9(2)	4.981(3)	7.087(9)	175.80(32)
24.3(3)	4.975(12)	7.066(27)	174.87(108)
27.2(4)	4.940(4)	7.048(10)	171.99(35)
31.3(4)	4.934(5)	7.052(11)	171.69(44)
33.6(5)	4.910(3)	7.019(7)	169.24(27)
36.8(6)	4.900(5)	7.011(12)	168.38(46)
40.1(3)	4.898(7)	6.978(16)	167.39(61)
42.4(2)	4.876(4)	6.983(11)	166.00(39)
45.1(2)	4.864(3)	6.970(9)	164.86(32)
47.2(3)	4.856(3)	6.961(9)	164.13(30)
52.7(3)	4.828(6)	6.924(12)	161.41(49)
53.7(4)	4.816(6)	6.923(10)	160.59(44)
55.6(9)	4.821(12)	6.899(22)	160.31(94)
57.0(7)	4.809(4)	6.906(8)	159.70(35)
58.1(6)	4.802(3)	6.900(5)	159.11(22)
59.6(5)	4.800(3)	6.895(6)	158.84(26)
60.7(5)	4.795(4)	6.889(8)	158.38(33)
62.3(4)	4.789(4)	6.881(8)	157.80(35)
64.4(4)	4.780(3)	6.872(6)	157.02(23)
65.4(4)	4.777(3)	6.868(5)	156.75(22)
66.8(5)	4.772(3)	6.862(6)	156.25(25)
68.7(5)	4.766(4)	6.851(8)	155.59(34)
70.0(5)	4.762(5)	6.846(9)	155.27(36)
72.5(9)	4.751(2)	6.837(4)	154.34(17)
73.0(9)	4.751(3)	6.835(5)	154.27(20)
74.4(8)	4.748(3)	6.831(5)	153.97(21)
75.6(8)	4.743(2)	6.825(4)	153.51(18)
77.2(6)	4.741(3)	6.819(5)	153.25(22)
79.0(5)	4.735(3)	6.810(6)	152.70(23)
81.1(5)	4.728(5)	6.797(10)	151.95(39)
81.9(5)	4.729(4)	6.800(7)	152.04(27)
82.4(5)	4.728(3)	6.799(6)	151.96(24)

The pressure was constrained by the EoS of gold published by Fei et al. (2007). The numbers in parentheses are uncertainties.

TABLE S6 Lattice parameters and unit cell volume of 25TiPv under high pressure.

$P$ (GPa)*	$a$ (Å)	$c$ (Å)	$V$ (Å <sup>3</sup> )
15.5(4)	3.596(2)	3.556(3)	45.98(7)
16.6(3)	3.583(4)	3.560(6)	45.71(14)
17.0(3)	3.582(2)	3.566(3)	45.75(7)
23.5(3)	3.563(2)	3.545(3)	44.99(6)
23.5(2)	3.559(2)	3.542(2)	44.86(5)
25.8(2)	3.549(2)	3.536(3)	44.53(7)
26.8(0)	3.545(2)	3.531(3)	44.38(5)
28.1(0)	3.539(2)	3.526(2)	44.15(5)
29.4(4)	3.530(1)	3.521(2)	43.89(4)
32.0(3)	3.519(4)	3.510(6)	43.46(13)
34.1(3)	3.514(3)	3.503(5)	43.25(9)
36.3(3)	3.507(3)	3.497(5)	43.00(10)
38.5(2)	3.498(2)	3.498(3)	42.81(5)
40.3(2)	3.490(2)	3.497(3)	42.59(6)
42.0(2)	3.484(2)	3.490(3)	42.37(5)
43.8(3)	3.471(4)	3.487(7)	42.01(13)
45.5(3)	3.464(2)	3.490(4)	41.86(7)
47.7(4)	3.458(3)	3.493(5)	41.76(9)
49.7(4)	3.450(5)	3.495(7)	41.61(14)
51.9(3)	3.439(5)	3.492(7)	41.30(14)
54.2(3)	3.434(4)	3.480(7)	41.04(14)
56.5(3)	3.425(5)	3.486(7)	40.89(14)
58.9(4)	3.417(5)	3.469(9)	40.52(16)
61.1(4)	3.420(4)	3.455(6)	40.41(12)
63.6(5)	3.408(4)	3.449(6)	40.04(11)

The pressure was constrained with the EoS of gold published by Fei et al. (2007). The numbers in parentheses are the uncertainties. The pressure uncertainties at 26.8 GPa and 28.1 GPa are 0.04 GPa and become zero after rounding.