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The structure of the metastable $K_{18}Ta_5Zr_5F_{63}$ phase

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Supporting Information

for NJCH

Table 1S. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) of $K_{18}Ta_5Zr_5F_{63}$

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}	Occ.
Ta1	0.34021(9)	0.32871(11)	3/4	0.0277(4)	0.69(2)
Zr1	0.34021(9)	0.32871(11)	3/4	0.0277(4)	0.31(2)
Ta2	2/3	1/3	3/4	0.0289(7)	0.52(2)
Zr2	2/3	1/3	3/4	0.0289(7)	0.48(2)
Zr3	0	0	1/4	0.0440(16)	1
K1	0.2674(4)	0.4220(4)	1/4	0.0369(13)	1
K2	0.5379(5)	0.4026(5)	1/4	0.0482(17)	1
K3	0.2295(10)	0.1487(8)	1/4	0.104(5)	1
F1	0.2440(9)	0.2843(9)	0.524 (3)	0.061(4)*	1
F2	0.402(2)	0.4231(19)	0.504 (7)	0.132(9)*	1
F3	0.3903(13)	0.2822(12)	0.543 (4)	0.099(6)*	1
F4	0.296(2)	0.409(3)	3/4	0.124(12)*	1
F5	0.227(4)	0.194(4)	3/4	0.081(14)*	0.5
F6	0.5727(16)	0.2609(16)	0.554 (5)	0.127(8)*	1
F7	0.091(3)	0.079(3)	0.051 (8)	0.092(12)*	0.5

Table 2S. Main geometric parameters (Å) of $K_{18}Ta_5Zr_5F_{63}$

Ta1—F3	1.89(2)	K1—F4	2.988(8)
Ta1—F3^{i}	1.89(2)	K1—F4^{xxiii}	2.988(8)
Ta1—F1	1.958(15)	K1—F6^{xxi}	2.60(3)
Ta1—F1^{i}	1.958(15)	K1—F6^{xxii}	2.60(3)
Ta1—F4	1.90(4)	K1—F1^{xi}	2.736(16)
Ta1—F5	2.18(6)	K1—F1	2.736(16)
Ta1—F2^{i}	2.04(4)	K1—F3^{xxii}	2.81(2)
Ta1—F2	2.04(4)	K1—F3^{xxi}	2.81(2)
Ta2—F6^{v}	1.87(3)	K1—F2	2.77(3)
Ta2—F6^{vi}	1.87(3)	K1—F2^{xi}	2.77(3)
Ta2—F6^{i}	1.87(3)	K1—Zr2^{x}	3.811(6)
Ta2—F6	1.87(3)	K1—Ta2^{x}	3.811(6)
Ta2—F6^{vii}	1.87(3)	K2—F2^{xi}	2.95(3)
Ta2—F6^{viii}	1.87(3)	K2—F2	2.95(3)
Zr3—F7^{xi}	1.89(4)	K2—F3^{xi}	2.92(2)
Zr3—F7^{xii}	1.89(4)	K2—F3	2.92(2)
Zr3—F7^{xiii}	1.89(4)	K2—F2^{x}	3.03(3)
Zr3—F7^{xiv}	1.89(4)	K2—F2^{xxiv}	3.03(3)
Zr3—F7^{xv}	1.89(4)	K2—F6^{viii}	3.01(3)
Zr3—F7	1.89(4)	K2—F6^{xxv}	3.01(3)
Zr3—F7^{xvi}	2.30(4)	K2—F4^{x}	3.10(4)
Zr3—F7^{iv}	2.30(4)	K2—F6	3.33(3)
Zr3—F7^{xvii}	2.30(4)	K2—F6^{xi}	3.33(3)
Zr3—F7^{xviii}	2.30(4)	K2—Ta1^{x}	4.050(7)
Zr3—F7^{xix}	2.30(4)	K3—F7	2.38(4)
Zr3—F7^{xx}	2.30(4)	K3—F7^{xi}	2.38(4)
		K3—F1	2.754(16)
		K3—F1^{xi}	2.754(16)

	K3—F1^{xxvi}	2.826(16)
	K3—F1^{iii}	2.826(16)
	K3—F5^{iii}	2.89(6)
	K3—F5^{xxiii}	3.030(15)
	K3—F5	3.030(15)
	K3—F3^{xi}	3.10(2)
	K3—F3	3.10(2)
	K3—F7^{xviii}	3.23(5)

Symmetry codes: (i) *x*, *y*, -*z*+3/2; (ii) *x*, *y*, *z*+1; (iii) *y*, -*x*+*y*, -*z*+1; (iv) *x*-*y*, *x*, *z*+1/2; (v) -*y*+1, *x*-*y*, -*z*+3/2; (vi) -*y*+1, *x*-*y*, *z*; (vii) -*x*+*y*+1, -*x*+1, -*z*+3/2; (viii) -*x*+*y*+1, -*x*+1, *z*; (ix) *x*-*y*+1, *x*, *z*+1/2; (x) -*x*+1, -*y*+1, -*z*+1; (xi) *x*, *y*, -*z*+1/2; (xii) -*x*+*y*, -*x*, *z*; (xiii) -*y*, *x*-*y*, *z*; (xiv) -*y*, *x*-*y*, -*z*+1/2; (xv) -*x*+*y*, -*x*, -*z*+1/2; (xvi) -*x*, -*y*, -*z*; (xvii) *y*, -*x*+*y*, *z*+1/2; (xviii) *y*, -*x*+*y*, -*z*; (xix) *x*-*y*, *x*, -*z*; (xx) -*x*, -*y*, *z*+1/2; (xxi) *x*-*y*, *x*, -*z*+1; (xxii) *x*-*y*, *x*, *z*-1/2; (xxiii) *x*, *y*, *z*-1; (xxiv) -*x*+1, -*y*+1, *z*-1/2; (xxv) -*x*+*y*+1, -*x*+1, -*z*+1/2; (xxvi) *y*, -*x*+*y*, *z*-1/2.

Table 3S. Main parameters of processing and refinement of $K_{18}Ta_5Zr_5F_{63}$ and K_3ZrF_7

T, K	Phase	Space group	Cell parameters (º, Å), Cell volume (Å^3)	R_{wp}, R_p (%), χ^2
153	$K_{18}Ta_5Zr_5F_{63}$	$P6_3/m$	*a* = 17.2600 (9), *c* = 5.8203 (3), *V* = 1501.6 (2)	9.51, 6.65, 2.43
183	$K_{18}Ta_5Zr_5F_{63}$	$P6_3/m$	*a* = 17.2933 (8), *c* = 5.8246 (3), *V* = 1508.5 (2)	9.25, 6.53, 2.37
213	$K_{18}Ta_5Zr_5F_{63}$	$P6_3/m$	*a* = 17.3236 (8), *c* = 5.8279 (3), *V* = 1514.7 (2)	8.86, 6.21, 2.27
243	$K_{18}Ta_5Zr_5F_{63}$	$P6_3/m$	*a* = 17.3491 (8), *c* = 5.8320 (3), *V* = 1520.2 (2)	8.65, 6.10, 2.21
273	$K_{18}Ta_5Zr_5F_{63}$	$P6_3/m$	*a* = 17.3770 (9), *c* = 5.8364 (3), *V* = 1526.2 (2)	8.60, 6.02, 2.19
303	$K_{18}Ta_5Zr_5F_{63}$	$P6_3/m$	*a* = 17.4023(9), *c* = 5.8430(3), *V* = 1532.4(2)	6.24, 4.57, 1.61
333	$K_{18}Ta_5Zr_5F_{63}$	$P6_3/m$	*a* = 17.4201(7), *c* = 5.8496(3), *V* = 1537.29(15)	6.20, 4.51, 1.60
363	$K_{18}Ta_5Zr_5F_{63}$	$P6_3/m$	*a* = 17.4468(8), *c* = 5.8557(3), *V* = 1543.62(16)	6.10, 4.47, 1.58
393	$K_{18}Ta_5Zr_5F_{63}$	$P6_3/m$	*a* = 17.4721(7), *c* = 5.8607(3), *V* = 1549.41(15)	5.95, 4.38, 1.53
423	$K_{18}Ta_5Zr_5F_{63}$	$P6_3/m$	*a* = 17.5006(8), *c* = 5.8673(3),	5.87, 4.33, 1.51

453	$K_{18}Ta_5Zr_5F_{63}$	$P6_3/m$	V = 1556.23(15)	6.34, 4.76, 1.62
			a = 17.5274(7), c = 5.8739(3), V = 1562.75(15)	
483	$K_{18}Ta_5Zr_5F_{63}$	$P6_3/m$	a = 17.5567(8), c = 5.8837(3), V = 1570.62(17)	5.82, 4.30, 1.49
513	$K_{18}Ta_5Zr_5F_{63}$	$P6_3/m$	a = 17.5824(8), c = 5.8952(3), V = 1578.29(16)	5.54, 4.19, 1.42
543	$K_{18}Ta_5Zr_5F_{63}$	$P6_3/m$	a = 17.5930(7), c = 5.9122(2), V = 1584.74(15)	5.05, 3.92, 1.29
	K_3ZrF_7	$Fm\bar{3}m$	a = 9.07(2), V = 746(5)	
573	$K_{18}Ta_5Zr_5F_{63}$	$P6_3/m$	a = 17.6022(8), c = 5.9340(3), V = 1592.26(18)	5.11, 4.03, 1.31
	K_3ZrF_7	$Fm\bar{3}m$	a = 9.073(3), V = 746.9(7)	
603	$K_{18}Ta_5Zr_5F_{63}$	$P6_3/m$	a = 17.609(7), c = 5.944(3), V = 1596(1)	4.70, 3.68, 1.19
	K_3ZrF_7	$Fm\bar{3}m$	a = 9.069(4), V = 746(1)	
633	K_3ZrF_7	$Fm\bar{3}m$	a = 9.0778(3), V = 748.1(6)	5.53, 4.34, 1.28

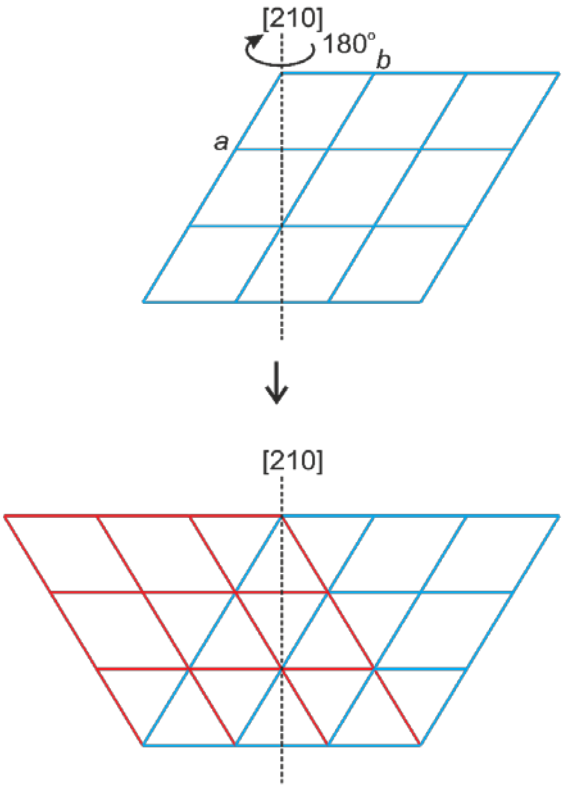

Figure 1S. The twinning mechanism in $K_{18}Ta_5Zr_5F_{63}$. The unit cell rotates around the [210] direction in real space. The ratio of the twinned block is close to 0.5:0.5.

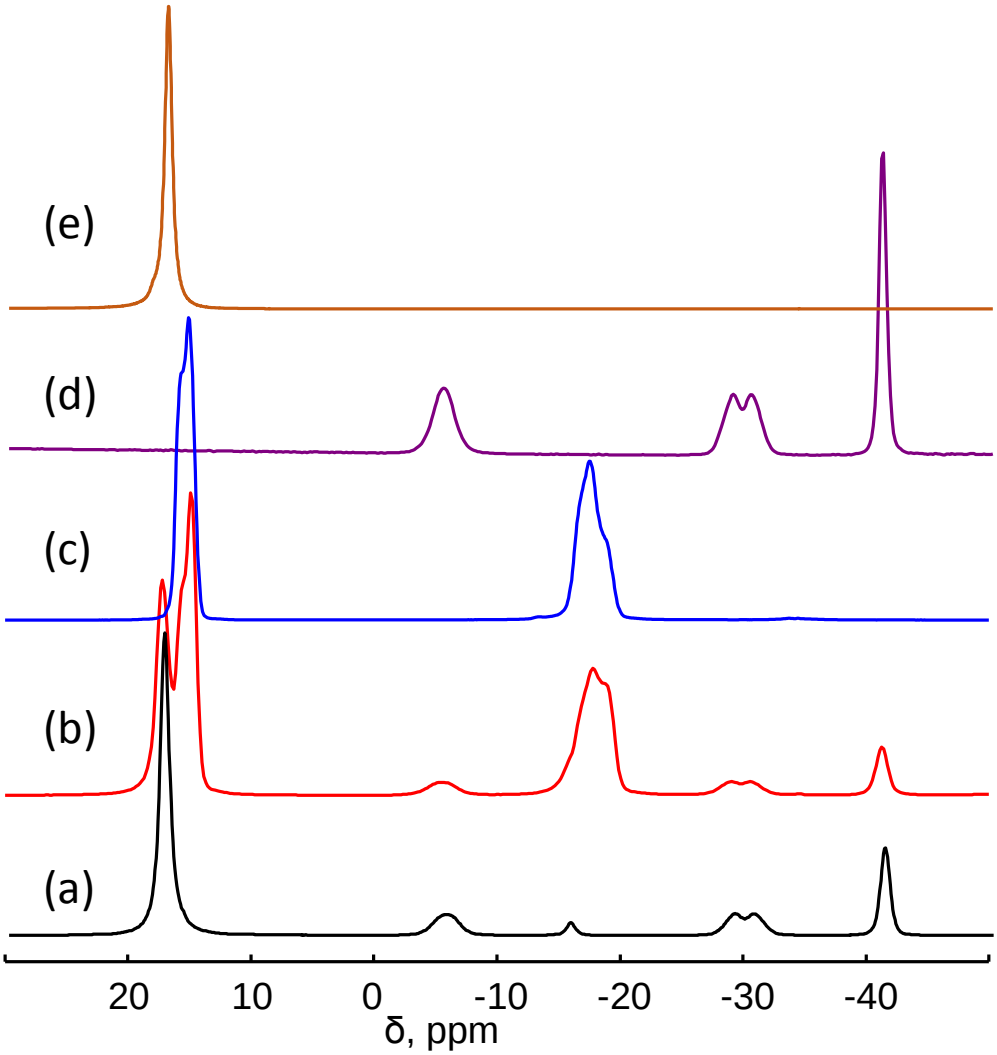

Figure 2S. ^{19}F MAS NMR spectra of the $K_{18}Ta_5Zr_5F_{63}$ sample measured a) three months after the synthesis, b) two months after the synthesis, and c) around ten days after the synthesis; and of d) K_2ZrF_6 and e) K_2TaF_7.

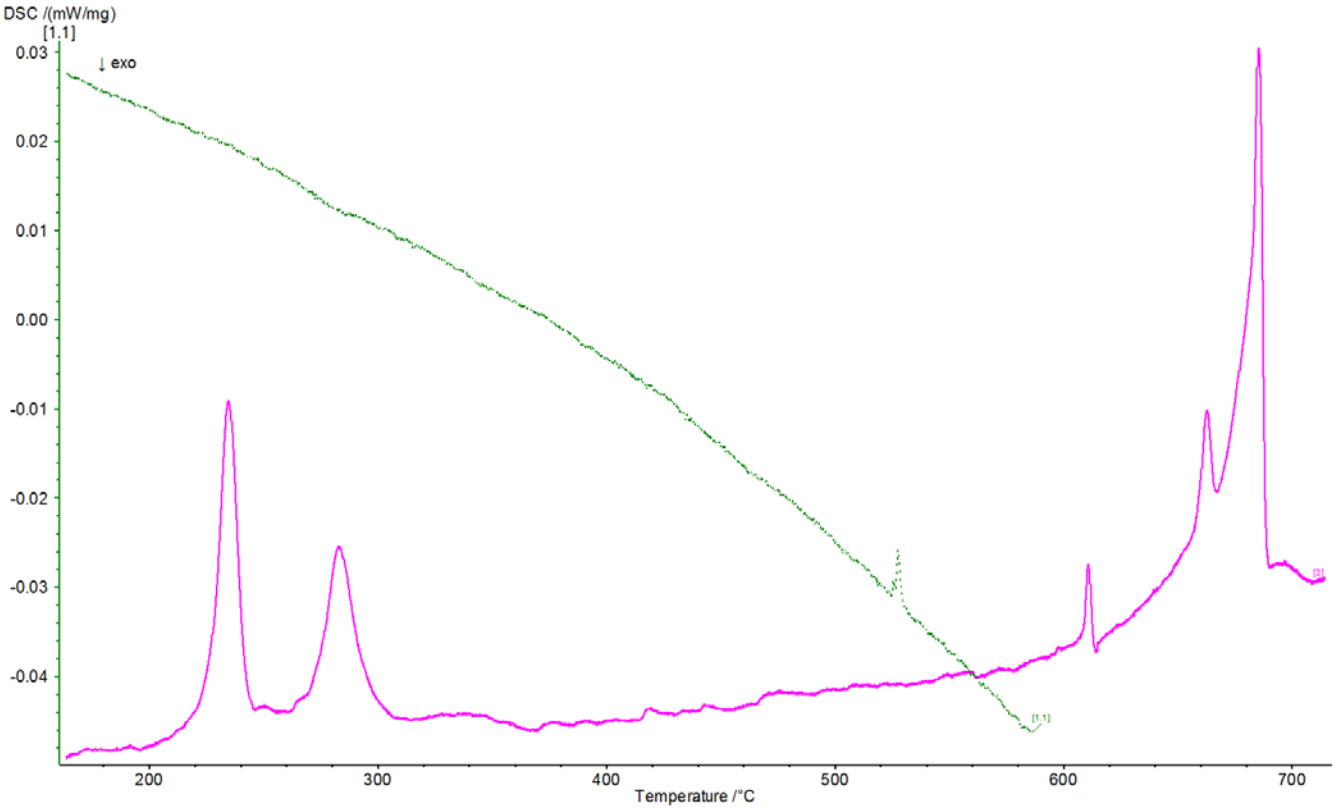

Figure 3S. DSC record of fresh sample of $K_{18}Ta_5Zr_5F_{63}$ (green dotted line) and three months old sample (violet line).