substance: Ti_nO_{2n-1} ($n \geq 3$)
property: crystal structure of Ti_5O_9

crystal structure: triclinic, space group $C_i^1 - P\bar{1}$, $Z = 2$. As for Ti_4O_7 there are two distinguishable strings of octahedra, labelled 5 – 3 – 1 – 3 – 5 and 6 – 4 – 2 – 4 – 6 (Fig. 1), and there are two phase transitions marked by discontinuities in the lattice parameters (Fig. 2).

transition parameters

T_{tr}	142 K (6 K wide)	upper transition	77M
ΔH_{tr}	135(5) cal mol^{-1}		
ΔS_{tr}	0.97 cal K^{-1} mol^{-1}		
T_{tr}	131K (4 K wide)	lower transition	
ΔH_{tr}	110(5) cal mol^{-1}		
ΔS_{tr}	0.85 cal K^{-1} mol^{-1}		

Report on additional crystallographic transition at ≈ 127 K corresponding to a change in superstructure without appreciable change in subcell parameters. This transition is also reported in conductivity data [83I].

lattice parameters

(distances in Å, angles in °)

a	5.569	5.577(2)	RT	first column [60A], second
b	7.120	7.127(2)		column [63A], [82L]
c	8.865	8.872(3)		
α	97.55	97.561(7)		
β	112.34	112.356(9)		
γ	108.50	108.524(7)		

interatomic distances
(in Å, at RT) (from [77M])

The symbols c, e, and f refer to Ti – Ti distances across a shared octahedral corner, edge, or face, respectively. The symbol b indicates Ti - Ti distances between rutile blocks.

Ti(1) –	O(2) (2×)	1.9543(9)
	O(3) (2×)	1.9666(9)
	O(4) (2×)	2.0164(11)
Average		1.979
O(2) –	O(3) (2×)	2.598(2)
O(2) –	O(3) (2×)	2.937(1)
O(2) –	O(4) (2×)	2.797(1)
O(2) –	O(4) (2×)	2.819(1)
O(3) –	O(4) (2×)	2.780(1)
O(3) –	O(4) (2×)	2.853(2)
Average		2.787
Ti(2) –	O(1)(2×)	2.0090(11)
	O(2)(2×)	1.9733(11)
	O(5)(2×)	2.0044(8)
Average		1.996

Ti(4) –	O(1)	1.9406(9)
	O(3)	1.9060(11)
	O(4)	1.9953(11)
	O(5)	1.9887(12)
	O(6)	2.0937(11)
	O(9)	2.0893(8)
Average		2.002
O(1) –	O(3)	2.830(1)
O(1) –	O(4)	2.979(1)
O(1) –	O(5)	2.690(2)
O(1) –	O(6)	2.959(1)
O(9) –	O(3)	2.843(1)
O(9) –	O(4)	2.712(2)
O(9) –	O(5)	2.920(1)
O(9) –	O(6)	2.696(1)

O(1) –	O(2)(2×)	2.765(2)
O(1) –	O(2)(2×)	2.865(2)
O(1) –	O(5)(2×)	2.690(2)
O(1) –	O(5)(2×)	2.979(1)
O(2) –	O(5)(2×)	2.802(1)
O(2) –	O(5)(2×)	2.824(1)
Average		2.820
Ti(3) –	O(1)	1.9073(12)
	O(2)	1.9264(10)
	O(3)	1.9756(9)
	O(6)	2.0342(9)
	O(7)	2.0673 (9)
	O(8)	2.0866(11)
Average		2.000
O(3) –	O(1)	2.769(2)
O(3) –	O(2)	2.598(2)
O(3) –	O(7)	2.928(1)
O(3) –	O(8)	2.705(1)
O(6) –	O(1)	2.986(2)
O(6) –	O(7)	2.693 (2)
O(6) –	O(8)	2.824(1)
O(1) –	O(2)	2.866(2)
O(1) –	O(7)	2.852(1)
O(8) –	O(2)	2.849(1)
O(8) –	O(7)	2.697(2)
Average		2.817

O(4) –	O(7)	2.809(1)
O(4) –	O(8)	2.908(1)
O(4) –	O(9)	2.712(2)
O(4) –	O(9)	2.878(1)
O(6) –	O(7)	2.681(1)
O(6) –	O(8)	3.000(2)
O(6) –	O(9)	2.696(1)
O(6) –	O(9)	2.698(1)
O(8) –	O(7)	3.039(2)
O(8) –	O(9)	2.947(2)
O(9) –	O(7)	2.648(1)
O(9) –	O(9)	2.581(1)
Average		2.800
Ti(1) –	Ti(4)c (2×)	3.5225(4)
	Ti(4)c (2×)	3.6078(4)
	Ti(6)c (2×)	3.4774(4)
	Ti(2)c (2×)	3.5590(2)
	Ti(3)e (2×)	2.9234(4)

O(4) –	O(3)	2.907(2)
O(4) –	O(6)	2.810(1)
O(5) –	O(3)	2.763(1)
O(5) –	O(6)	2.780(2)
Average		2.824
Ti(5) –	O(5)	1.8425(12)
	O(6)	2.0517(10)
	O(7)	1.9915(9)
	O(8)	1.9394(9)
	O(9)	2.0384(10)
Average		2.003
O(9) –	O(5)	3.087(2)
O(9) –	O(6)	2.698(1)
O(9) –	O(7)	2.648(1)
O(9) –	O(8)	2.838(2)
O(7) –	O(5)	2.942(2)
O(7) –	O(6)	2.681(1)
O(7) –	O(7)	2.573(1)
O(7) –	O(8)	2.895(1)
O(7) –	O(8)	2.697(2)
O(7) –	O(6)	2.693(2)
O(5) –	O(8)	2.833(1)
O(5) –	O(6)	3.027(2)
Average		2.801
Ti(6) –	O(4)	1.8803(8)
	O(6)	2.1314(10)
	O(7)	2+0027 (11)
	O(8)	1.8563(11)
	O(9)	1.9799(11)
	O(9)	2.1878(11)
Average		2.006
Ti(4) –	Ti(3)c	3.4660(4)
	Ti(3)c	3.5527(5)
	Ti(3)c	3.5653(5)
	Ti(5)c	3.5540(5)
	Ti(5)c	3.7704(5)
	Ti(1)c	3.5225(4)
	Ti(1)c	3.6078(4)
	Ti(2)e	2.9191(4)
	Ti(6)e	3.0362(4)
	Ti(5)cb	3.8210(5)
	Ti(6)eb	3.1114(4)
Ti(5) –	Ti(6)c	3.5561(4)
	Ti(6)c	3.5622(4)
	Ti(3)e	2.9988(4)
	Ti(4)c	3.5540(5)
	Ti(4)c	3.7704(5)
	Ti(2)c	3.4668(3)
	Ti(6)fb	2.8323 (5)

Ti(2) –	Ti(3)c (2×)	3.5324(4)
	Ti(3)c (2×)	3.6109(4)
	Ti(1)c (2×)	3.5590(2)
	Ti(5)c (2×)	3.4668(3)
	Ti(4)e (2×)	2.9191(4)
Ti(3) –	Ti(6)c	3.5349(5)
	Ti(6)c	3.7894(5)
	Ti(4)c	3.4660(4)
	Ti(4)c	3.5527(5)
	Ti(4)c	3.5653(5)
	Ti(1)e	2.9234(4)
	Ti(2)c	3.5324(4)
	Ti(2)c	3.6109(4)
	Ti(5)e	2.9988 (4)
	Ti(6)cb	3.8036(5)
	Ti(5)eb	3.1210(4)
	Ti(5)eb	3.2586(6)
	Ti(6)cb	3.3900(5)
	Ti(4)cb	3.8210(5)
	Ti(3)eb	3.1210(4)
Ti(6) –	Ti(5)c	3.5561(4)
	Ti(5)c	3.5622(4)
	Ti(4)e	3.0362(4)
	Ti(3)c	3.5349(5)
	Ti(3)c	3.7894(5)
	Ti(1)c	3.4774(4)
	Ti(5)fb	2.8323(5)
	Ti(6)eb	3.2788(6)
	Ti(5)cb	3.3900(5)
	Ti(3)cb	3.8036(5)
	Ti(4)eb	3.1114(4)

electrostatic charges at the Ti-ions
(in units of *e*) (from [77M])

*e**/*e* of:	*T* = 298 K	135 K	115 K
Ti(1)	3.85	3.91	3.92
Ti(2)	3.65	3.60	3.65
Ti(3)	3.60	3.60	3.56
Ti(4)	3.57	3.60	3.59
Ti(5)	3.56	3.52	3.50
Ti(6)	3.52	3.52	3.52
Average	3.60	3.60	3.59

calculated from Ti – O bond lengths. There is no clearcut evidence of low-temperature electron condensation into bipolarons as in Ti_4O_7, since there is no marked change in the partial cation charges with temperature

References:

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Fig. 1.

Ti_5O_9. Structure showing two distinguishable strings [77M]. Inset shows the rutile-derived cell.

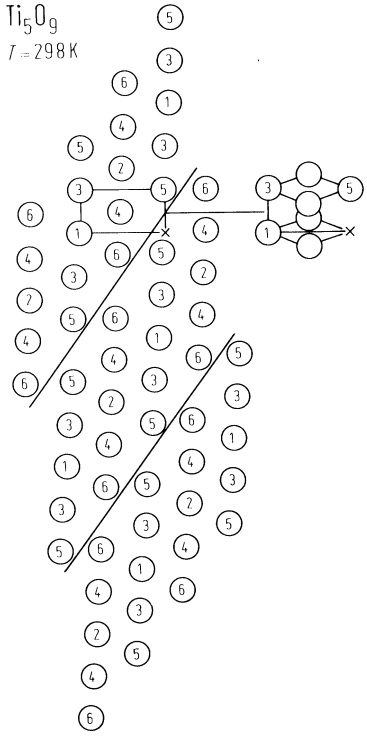

Fig. 2.

Ti_5O_9. Lattice parameters vs. temperature [77M].