Zirconium Tungstate

INTRODUCTION

Zirconium Tungstate is a complex oxide that exhibits the unusual property of contracting, rather than expanding, as its temperature rises from near absolute zero to its decomposition-temperature near I050°K (780°C). Throughout this range, Zirconium Tungstate has cubic symmetry, so that its thermal expansion is the same in any direction. Near 428°K (155°C), Zirconium Tungstate undergoes a second-order phase transformation to a disordered phase of higher symmetry, called β-Zirconium Tungstate to distinguish it from the α-phase, the form stable below 428°K. When exposed to pressure at room temperature, α-Zirconium Tungstate converts to a denser polymorph, called the γ-phase. This phase persists at atmospheric pressure, but reverts to the α-form when heated.

TYPICAL COMPOSITION

Table 1. Typical Chemistry (On as received basis ppm except where noted. Nominal Purity 99.5 (Zr+Hf)		
Element		Analysis
Al	Aluminum	<200
Fe	Iron	<200
Hf	Hafnium	<100
Si	Silicon	<400
Ti	Titanium	<100

FORMULA

ZrW_2O_8.

DESCRIPTION

A fine white to light green powder.

PARTICLE SIZE

The typical median is 16 microns.

BULK DENSITY

Approximately 5072-5355 kg/m^3

PACKAGING

Double plastic bags inside metal drums or polyethylene containers Polyethylene jars inside metal drums or polyethylene containers.

HANDLING

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Zirconium tungstate is inert. Avoid personal contact and dust generating conditions. Store in a dry location away from combustibles. See MSDS for further information.

PHYSICAL PROPERTIES

Table 1. α-Zirconium Tungstate			
Appearance	White powder		
Formula	ZrW_2O_8		
Formula mass	586.91 g		
Crystal symmetry	Cubic		
Formula units per cell	4		
*Powder diffraction-pattern, 293K, three strongest peaks	h k l	d,nm	I/I max
	210	0.40957	100
	211	0.37388	78
	321	0.24476	34
Cell parameter	0.915993(5)nm, 293°K		
a–1 Transition temperature, 0.1 MPa	428°K		
Space group	P2, 3, 0°K<T≤428°K		
Density	5072 $kg.m^{-3}$, 293°K		
Bulk modulus	69.4 GPa, 300°K		
Coefficient of thermal expansion	See Figure 1		
Average value	-8.8×10^{-6} K^{-1}, 0°K<T<400°K		
Dielectric constant	See Figures 2, 4		
Loss tangent	See Figures 3, 4		
Conductivity, electrical	See Figure 5		
Refractive index, natural light	1.669±.002		
Solubility in water	<0.1 $mg.1^{-1}$, 293°K		
Reaction with boiling (0.1 MPa) 2N aqueous hydrochloric acid	None		
Reaction with boiling (0.1 MPa) 2N aqueous sodium hydroxide	Decomposes		
Decomposition temperature in air (0.1 MPa)	1050°K		
*The complete listing of powder diffraction-pattern peaks will be sent on request.			

Table 2. β-Zirconium Tungstate			
Appearance	White powder		
Crystal symmetry	Cubic		
Formula units per cell	4		
*Powder diffraction-pattern, 509°K, three strongest peaks	h k l	d,nm	I/I max
	210	0.4055	100
	211	0.3730	65
	321	0.2442	50
Cell parameter	0.91371(5) nm, 483°K		

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α–β Transition temperature	428°K	
Space group	Pa 3	
Density	5110 kg.m^{-3}, 483°K	
Coefficient of thermal expansion	See Figure 1	
Average value	-4.9 x 10^{-6} K^{-1}, 430°K<T<950°K	
Dielectric constant	See Figures 2, 4	
Loss tangent	See Figures 3, 4	
Conductivity, electrical	See Figure 5	

Table 3. γ-Zirconium Tungstate

Transition pressure	210 MPa, 293°K		
Volume-change at transition	5.77 x 10^{-3} liter per gram formula-mass		
Crystal symmetry	Orthorhombic		
Formula units per cell	12		
*Powder diffraction pattern, 293°K, three strongest peaks	h k l	d,nm	I/I max
	160	0.40355	100
	201	0.40424	93
	231	0.36883	75
Cell parameters, 0.1 MPa	a: 0.9069 nm		
	b: 2.7020 nm		
	c: 0.8912 nm, 293°K		
Density, 0.1 MPa	5355 kg.m^{-3}, 293°K		
Bulk modulus, 0.1 MPa	68.0 GPa. 300°K		
Temperature of reversion to cubic form	393°K		
Coefficient of thermal expansion, 0.1 MPa	a: -1.88 x 10^{-6} K^{-1}, 293°K		
	b: -0.68 x 10^{-6} K^{-1}, 293°K		
	c: -0.92 x 10^{-6} K^{-1}, 293°K		

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Figure 1. Thermal Expansion of Zirconium Tungstate

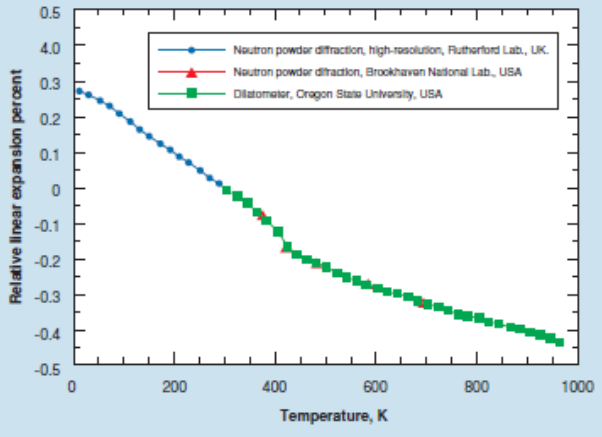

Figure 2. Frequency dependence of dielectric constant of zirconium tungstate at four temperatures

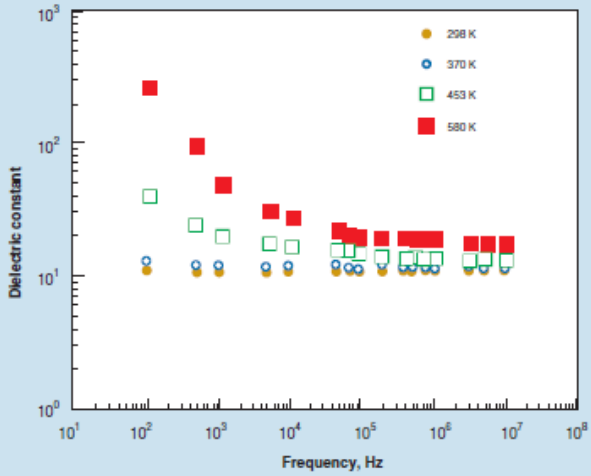

Figure 3. Frequency dependence of dielectric loss-tangent of zirconium tungstate at four temperatures

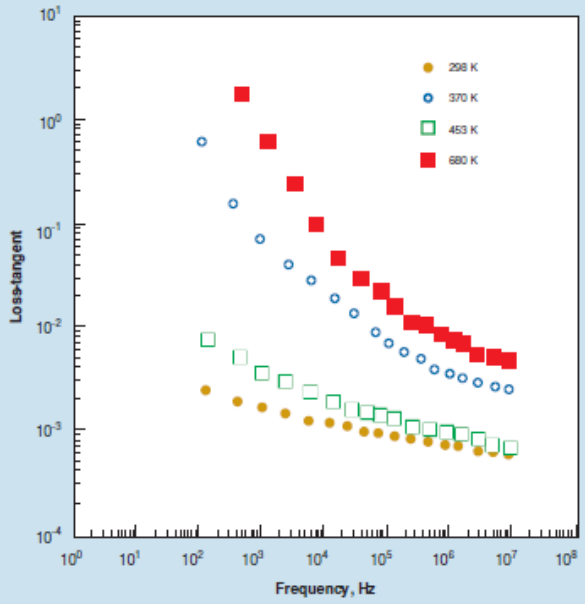

Figure 4. Temperature dependence of dielectric constant and loss-tangent of zirconium tungstate measured at 1kHz

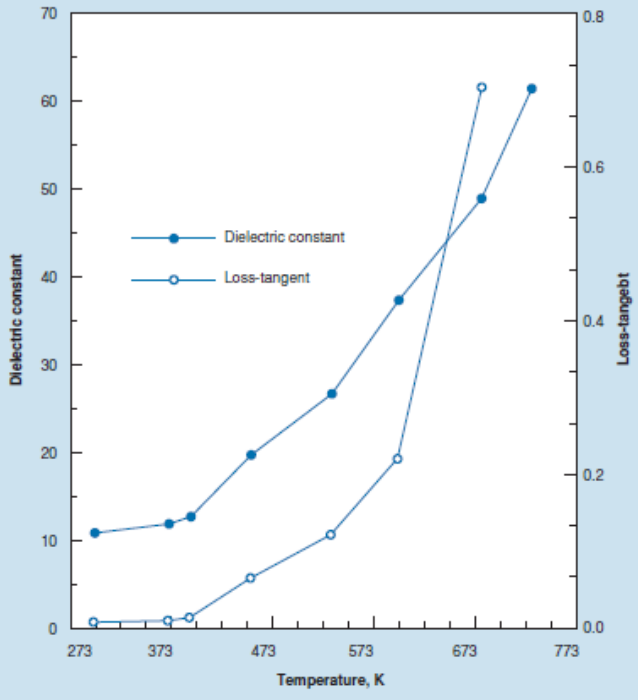

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Figure 5. Temperature dependence of electrical conductivity of zirconium tungstate, deduced from impedance spectroscopy measurements.

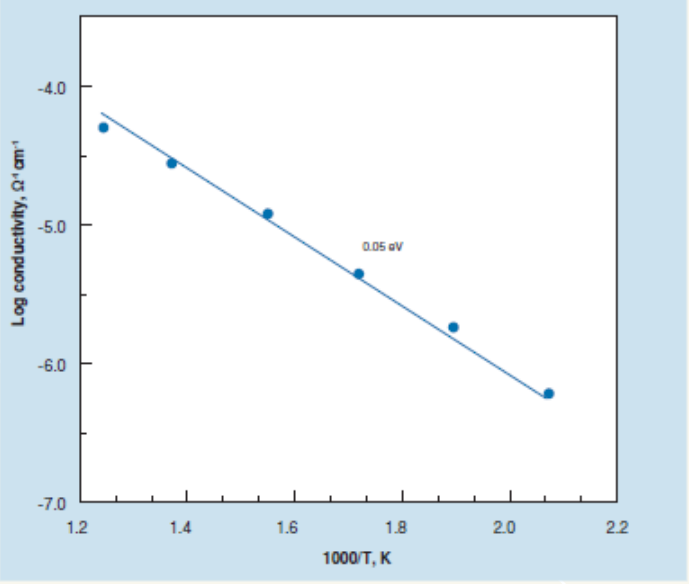

Table 4. Diffraction Pattern of α-ZrW_2O_8				
h	k	l	d-value, nm	Relative intensity
1	1	1	0.52875	14
2	0	0	0.45791	9
2	1	0	0.40957	100
2	1	1	0.37388	78
2	2	0	0.32379	17
2	2	1	0.30527	9
3	1	0	0.28961	17
3	1	1	0.27613	28
3	2	0	0.25400	18
3	2	1	0.24476	34
4	0	0	0.22896	3
4	0	1	0.22212	7
3	2	2	0.22212	4
3	3	1	0.21010	5
4	2	0	0.20478	5
4	2	1	0.19985	17
3	3	2	0.19525	3
4	2	2	0.18694	17

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4	3	0	0.18316	7
5	1	0	0.17961	5
4	3	1	0.17961	11
5	1	1	0.17625	15
3	3	3	0.17625	9
5	2	0	0.17006	10
4	3	2	0.17006	7
5	1	2	0.16721	2
5	2	1	0.16721	3
4	4	0	0.16190	11
5	2	2	0.15942	1
4	4	1	0.15942	4
5	3	0	0.15706	7
5	3	1	0.15480	1
4	4	2	0.15264	2
6	1	0	0.15056	1
5	3	2	0.14857	6
6	1	1	0.14857	5
5	2	3	0.14857	5
6	2	1	0.14303	7

Table 5. Diffraction Pattern of -y-ZrW2O8

h	k	l	d-value	Relative intensity
0	2	0	1.35187	1
0	1	1	0.84709	17
1	2	0	0.75316	1
0	4	0	0.67593	7
1	3	0	0.63928	2
1	0	1	0.63596	4
0	3	1	0.63398	11
1	1	1	0.61906	3
1	2	1	0.57546	6
1	4	0	0.54197	1
0	4	1	0.53873	2
1	3	1	0.51962	9
1	4	1	0.46318	4
0	5	1	0.46241	5
2	0	0	0.45347	6

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0	6	0	0.45062	18
2	1	0	0.44723	1
0	0	2	0.44600	11
2	2	0	0.42993	1
0	2	2	0.42355	1
1	5	1	0.41196	3
2	0	1	0.40424	93
1	6	0	0.40355	100
0	6	1	0.40221	3
1	0	2	0.40023	2
2	1	1	0.39979	5
0	3	2	0.39973	60
1	1	2	0.39591	3
1	2	2	0.38376	2
2	4	0	0.37658	1
2	3	1	0.36883	75
1	6	1	0.36768	51
1	3	2	0.36578	53
1	7	0	0.35536	3
0	7	1	0.35444	3
2	5	0	0.34747	6
2	4	1	0.34693	1
1	4	2	0.34438	1

Table 6. Diffraction Pattern of γ-ZrW_2O_8

h	k	l	d-value	Relative intensity
0	5	2	0.34407	5
0	8	0	0.33797	2
1	7	1	0.33013	6
2	5	1	0.32377	1
1	5	2	0.32170	6
2	6	0	0.31964	6
2	0	2	0.31798	10
0	6	2	0.31699	9
1	8	0	0.31669	1
0	8	1	0.31604	4
2	1	2	0.31580	23
2	2	2	0.30953	5
2	3	2	0.29986	24

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1	6	2	0.29924	3
1	8	1	0.29844	1
0	1	3	0.29555	8
2	7	0	0.29404	4
0	7	2	0.29198	1
0	2	3	0.29039	8
3	0	1	0.28632	1
1	9	0	0.28518	1
0	9	1	0.28470	1
1	0	3	0.28254	4
0	3	3	0.28236	9
1	1	3	0.28101	4
3	2	1	0.28011	2
2	7	1	0.27926	2
1	7	2	0.27793	9
1	2	3	0.27656	1
3	4	0	0.27597	1
2	5	2	0.27410	2
3	3	1	0.27288	34
0	4	3	0.27217	2
1	9	1	0.27163	26
0	10	0	0.27037	1
1	3	3	0.26960	12
3	4	1	0.26364	2
1	4	3	0.26068	3
0	5	3	0.26054	6
2	6	2	0.25981	3
2	8	1	0.25928	3
1	10	0	0.25910	4

Table 7. Diffraction Pattern of γ-ZrW_2O_8

h	k	l	d-value	Relative intensity
0	10	2	0.25875	4
1	8	2	0.25822	2
3	6	0	0.25105	13
1	5	3	0.25042	1
3	1	2	0.24918	2
0	9	2	0.24916	10

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1	10	1	0.24882	1
2	0	3	0.24865	8
0	6	3	0.24818	5
2	2	3	0.24455	2
3	6	1	0.24166	15
3	3	2	0.24112	8
2	9	1	0.24112	13
1	9	2	0.24026	9
2	3	3	0.23969	7
1	6	3	0.23938	4
1	11	0	0.23724	3
2	4	3	0.23336	1
2	8	2	0.23159	3
3	7	1	0.23001	1
1	11	1	0.22927	2
1	7	3	0.22804	5
3	5	2	0.22710	2
4	0	0	0.22674	8
4	1	0	0.22594	3
2	5	3	0.22591	2
0	12	0	0.22531	4
0	2	4	0.22003	2
4	3	0	0.21989	3
1	12	0	0.21866	2
2	9	2	0.21837	1
2	6	3	0.21771	1
4	2	1	0.21690	1
1	8	3	0.21677	5
4	4	0	0.21497	1
1	2	4	0.21382	4
4	3	1	0.21349	1
3	9	0	0.21309	1
1	12	1	0.21238	1
3	0	3	0.21199	1
1	3	4	0.21056	1
3	7	2	0.21002	4
4	5	0	0.20910	8

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Table 8. Diffraction Pattern of γ-ZrW_2O_8				
h	k	l	d-value	Relative intensity
4	4	1	0.20898	1
3	9	1	0.20726	1
3	3	3	0.20635	1
1	4	4	0.20623	3
2	10	2	0.20598	6
1	9	3	0.20581	2
4	5	1	0.20358	2
1	13	0	0.20272	2
4	6	0	0.20254	2
3	4	3	0.20227	1
4	0	2	0.20212	1
2	12	0	0.20178	3
3	10	0	0.20153	1
3	8	2	0.20111	3
0	12	2	0.20111	2
2	8	3	0.20028	1
2	0	4	0.20011	1
0	6	4	0.19987	3
2	1	4	0.19957	1
2	2	4	0.19796	2
1	13	1	0.19768	1
4	6	1	0.19752	2
3	5	3	0.19736	2
4	3	2	0.19722	15
2	12	1	0.19680	9
3	10	1	0.19658	3
1	12	2	0.19634	1
2	3	4	0.19535	1
1	10	3	0.19534	1
1	6	4	0.19518	1
2	11	2	0.19447	1
4	4	2	0.19365	2
3	9	2	0.19227	10
2	4	4	0.19188	10
3	6	3	0.19182	2
2	9	3	0.19155	1
4	7	1	0.19100	1

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3	11	0	0.19071	1
4	5	2	0.18933	1
2	13	0	0.18905	1
0	13	2	0.18849	1
4	8	0	0.18829	1

Table 9. Diffraction Pattern of γ-ZrW_2O_8

h	k	l	d-value	Relative intensity
2	5	4	0.18767	6
3	l1	1	0.18650	2
0	8	4	0.18613	1
3	7	3	0.18584	3
1	11	3	0.18544	4
2	13	1	0.18494	3
1	14	1	0.18479	3
1	13	2	0.18455	3
4	6	2	0.18442	2
4	8	1	0.18423	2
2	12	2	0.18384	2
2	10	3	0.18302	1
2	6	4	0.18289	9
1	8	4	0.18233	2
3	12	0	0.18066	1
4	0	3	0.18030	2
4	1	3	0.17990	2
3	8	3	0.17958	3
0	12	3	0.17958	2
3	0	4	0.17946	6
3	1	4	0.17907	3
0	9	4	0.17906	1
4	2	3	0.17871	3
0	1	5	0.17801	3
3	2	4	0.17790	5
5	0	1	0.17775	1
0	2	5	0.17687	1
4	3	3	0.17679	2
0	15	1	0.17668	3
5	2	1	0.17624	1

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1	12	3	0.17616	6
1	9	4	0.17567	2
1	0	5	0.17505	1
0	3	5	0.17500	3
2	11	3	0.17480	1
1	1	5	0.17468	3
5	3	1	0.17439	9
4	4	3	0.17421	3
2	13	2	0.17405	5
1	14	2	0.17393	3
1	2	5	0.17360	3
3	4	4	0.17345	3

Table 10. Diffraction Pattern of γ-ZrW_2O_8

h	k	l	d-value	Relative intensity
1	15	1	0.17342	10
3	9	3	0.17321	5
0	4	5	0.17249	4
2	8	4	0.17219	2
0	10	4	0.17203	1
5	4	1	0.17191	1
1	3	5	0.17183	1
4	5	3	0.17104	3
4	10	1	0.17053	5
0	13	3	0.17042	5
3	5	4	0.17032	1
1	4	5	0.16946	1
1	10	4	0.16902	2
0	16	0	0.16898	3
5	5	1	0.16886	1
3	13	1	0.16827	3
5	6	0	0.16827	7
5	0	2	0.16803	1
4	9	2	0.16770	6
2	15	0	0.16750	2
1	13	3	0.16749	1
3	12	2	0.16744	3
4	6	3	0.16739	4

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2	12	3	0.16696	1
3	10	3	0.16682	1
5	2	2	0.16674	1
3	6	4	0.16672	3
1	5	5	0.16654	2
1	16	0	0.16612	1

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For an interpretation of the negative normal expansion of zirconium tungstate in light of its crystal structure, see TA. Mary, J.S .O. Evans, T. Vogt, A. W Sleight, “Negative Thermal Expansion From 0.3K to 1050 Kelvin in ZrW_2O_8,” Science, Vol. 272, 5 April 1996, pp. 90–92.

For a more detailed structure-based interpretation of zirconium tungstate's negative expansion, for structural data on the β-phase and for data on electrical properties, see “Negative Thermal Expansion in ZrW_2O_8, and HfW_2O_8”, J.S.O. Evans, T.A. Mary, T Vogt, M.A. Subramaniam and A.W Sleight, Chemistry of Materials Vol. 8, No. 12, pp. 2809–2823.

For a description and interpretation of the structure of the zirconium tungstate polymorph formed at high pressure see “Compressibility, phase transitions, and oxygen immigration in Zirconium Tungstate, ZrW_2O_8,”, J.S.O. Evans, Z. Hu, J.D. Jorgensen, D.N Argyriou, S. Short, A. W. Sleight, Science, Vol. 275, 3 January 1997, pp. 61–65.

For information on the thermal stability of zirconium tungstate, see “Condensed Phase Relations in the Systems ZrO_2-WO_2-WO_3 and HfO_2-WO_2-WO_3”, L. L. Y. Chang, M.G. Scroger, and B. Philips, J. Am. Cer. Soc., Vol. 50, No.4, 1967, pp. 211-215, quoted in Phase Diagrams for Ceramists 1975 Supplement, Ernest M. Levin and Howard F. McMurdie, Ed.s, The American Ceramic Society, Columbus, Ohio, p. 173, Fig. 4459.

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