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Crystal structure and thermodynamic properties of cesium tantalum tungsten oxide

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Abstract

In the present work temperature dependence of heat capacity of cesium tantalum tungsten oxide has been measured first in the range from 7 to 350 K and then between 330 and 630 K, respectively, by precision adiabatic vacuum and dynamic calorimetry. The experimental data were used to calculate standard thermodynamic functions, namely the heat capacity $C_p^{\circ}(T)$, enthalpy $H^{\circ}(T) - H^{\circ}(0)$, entropy $S^{\circ}(T) - S^{\circ}(0)$ and Gibbs function $G^{\circ}(T) - H^{\circ}(0)$, for the range from $T \rightarrow 0$ to 630 K. The structure of CsTaWO₆ is refined by the Rietveld method: space group F d3m, Z=8, a = 10.3793(2) Å, V = 1118.14(4) Å³. The high-temperature X-ray diffraction was used for the determination of temperature of phase transition and coefficient of thermal expansion.

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1. Introduction

Materials with the pyrochlore structure have been extensively studied for a range of applications including their use as adsorbents [1,2], radioactive waste form materials [3–5], as fast ion conductors [6], as Li-battery electrodes and, more recently, for photocatalytic splitting of water [7–10]. The pyrochlore structure type is also represented in a wide range of natural occurrences by the mineral group of pyrochlore, microlite, betafite and stibiconite [11].

The ideal defect pyrochlore structure has cubic symmetry (space group F d3m) and stoichiometry $A_2M_2X_6X'$ where A is a large, low valent cation (*e.g.* lanthanide or alkali metal or alkaline earth cation) and M is a smaller cation that can adopt octahedral coordination (*e.g.* Ti^{4+} , Zr^{4+} , W^{6+} , Sb^{6+}). Typically X is O^{2-} while X' may be an anion such as O^{2-} , OH^- or F^- .

The goals of this work include calorimetric determination of the temperature dependence of the heat capacity $C_p^\circ = f(T)$ of cesium tantalum tungsten oxide from 7 to 630 K, detection of

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the possible phase transitions, and calculation of the standard thermodynamic functions $C_p^{\circ}(T)$, $H^{\circ}(T) - H^{\circ}(0)$, $S^{\circ}(T) - S^{\circ}(0)$ and $G^{\circ}(T) - H^{\circ}(0)$ in the range from $T \to 0$ to 630 K.

2. Experimental

2.1. Sample

Cesium tantalum tungsten oxide was prepared by the solidstate reaction between tungsten oxide, tantalum oxide and cesium nitrate [12]. The synthesis was performed in a porcelain crucible, into which the reaction mixture with the atomic ratio 1Cs:1W:1Ta was loaded. The mixture was calcined at 1073 K for 50 h, undergoing regrinding every 10 h.

For structural investigations, an X-ray diffraction pattern of a CsTaWO₆ sample was recorded on a Shimadzu X-ray diffractometer XRD-6000 (Cu K α radiation, geometry θ -2 θ) in the 2 θ range from 10° to 120° with scan increment of 0.02°. Rietveld analysis and structure refinement [13] were carried out using RIETAN-94 software [14]. The X-ray data and estimated impurity content (0.5–1 wt%) in the substance led us to conclude that the cesium tantalum tungsten oxide sample studied was an individual crystalline compound. The high-temperature X-ray

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diffraction was carried out on a Shimadzu X-ray diffractometer XRD-6000 using Sample Heating Attachment HA-1001.

2.2. Apparatus and measurement procedure

To measure the heat capacity C_p° of the tested substance in the range from 7 to 350 K a BKT-3.0 automatic precision adiabatic vacuum calorimeter with discrete heating was used. The calorimeter design and the operation procedure were described earlier [15,16]. The calorimeter was tested by measuring the heat capacity of high-purity copper and reference samples of synthetic corundum and K-2 benzoic acid. The analysis of the results showed that measurement error of the heat capacity of the substance at helium temperatures was within $\pm 2\%$, then it decreased to $\pm 0.5\%$ as the temperature was rising to 40 K, and was equal to $\pm 0.2\%$ at T > 40 K. Temperatures of phase transitions can be determined with the error of ± 0.02 K.

To measure the heat capacity of the sample between 330 and 630 K an automatic thermo-analytical complex (ADKTTM) a dynamic calorimeter operating by the principle of triple thermal bridge - was employed [17,18]. The device design and the measurement procedure of the heat capacity, temperatures and enthalpies of phase transitions were demonstrated in detail in the above-mentioned papers. The reliability of the calorimeter operation was checked by measuring the heat capacity of the standard sample of synthetic corundum as well as the thermodynamic characteristics of fusion of indium, tin and lead. As a result, it was found that the calorimeter and the measurement technique allow one to obtain the heat capacity values of the substances in solid and liquid states with the maximum error of $\pm 1.5\%$ and the phase transition temperatures within *ca*. ± 0.5 K. Since the heat capacity of the examined compound was also measured between 330 and 350K in the adiabatic vacuum calorimeter with the error of $\pm 0.2\%$ and the conditions of measurements in the dynamic device were chosen so that in the above temperature interval the C_p° values measured with the use of both calorimeters coincided, it was assumed that at T > 350 K the heat capacity was determined with the error of 0.5-1.5%. The data on the heat capacity of the object under study were obtained in the range from 330 to 630 K at the average rate of heating of the calorimeter and the substance of 0.0333 K/s.

3. Results and discussion

3.1. Crystal structure

The structure of CsTaWO₆ was refined assuming space group F d3m. The initial model included the atomic coordinates in the structure of CsNbWO₆ [12]. The details of the X-ray diffraction experiment and structure refinement data are listed in Table 1.

Fig. 1 represents the measured, simulated, and difference Xray diffraction patterns for CsTaWO₆, as well as a pattern of lines corresponding to reflection maxima. There is a good agreement between the measured and simulated patterns. Table 2 lists the coordinates of the atoms and their isotropic thermal parameters.

Table 1

Details of the X-ray diffraction experiment and the results of the structure refinement for $CsTaWO_6$

Space group	F d3m	
Ζ	8	
2θ range (°)	10-120	
a (Å)	10.3793(2)	
$V(Å^3)$	1118.14(4)	
Number of reflections	73	
Number of refined parameters:		
Structural parameters	4	
Others	20	
Final values (%):		
$R_{wp}; R_p$	3.22; 2.31	

$$\mathbf{R}_{wp} = \left\{ \frac{\sum_{w_i [y_{iobs} - y_{icalc}]^2}}{\sum_{w_i [y_{iobs}]^2}} \right\}^{1/2}; \quad \mathbf{R}_p = \frac{\sum_{w_i [y_{iobs} - y_{icalc}]}}{\sum_{w_i [y_{iobs}]^2}}.$$



Fig. 1. Fragments of (1) observed, (2) simulated, and (4) difference X-ray diffraction patterns for CsTaWO₆ and (3) Bragg reflections. The simulated pattern is shifted relative to the observed pattern.

The refined model yielded positive isotropic thermal parameters B for all atoms. The Ta/W–O bond lengths are 1.966 ± 0.001 Å, and Cs–O bond lengths are 3.186 ± 0.004 Å.

Fig. 2 represents a fragment of the CsTaWO₆ structure. The (Ta/W)O₆ octahedra share corners to form a three-dimensional framework possessing tunnels running down the *c*-axis in which the Cs cations are located. The Ta/W cations are located in the 16c Wyckoff sites (0, 0, 0) and the oxygen atoms are in 48f sites (x, 1/8, 1/8). The location of the cesium cations is in the 8b sites (3/8, 3/8, 3/8).

Table 2										
Coordinates	and	isotropic	thermal	parameters	of	atoms	in	the	structure	of
CsTaWO ₆										

Atom	Site	x	у	z	Occ	$B(Å^2)$
Cs	8b	0.375	0.375	0.375		1.52(4)
Та	16c	0	0	0	0.5	0.75(2)
W	16c	0	0	0	0.5	0.75(2)
0	48f	0.3180(4)	0.125	0.125		0.75(2)



Fig. 2. Fragment of the structure of CsTaWO₆.

3.2. Heat capacity

The C_p° measurements were carried out between 7 and 630 K. The masses of the sample loaded in the calorimetric ampoules of the BKT-3.0 and ADKTTM devices were 2.2184 and 2.1423 g, respectively. In the BKT-3.0 calorimeter, 121 experimental C_p° values were obtained in two series of experiments. The heat capacity of the sample varied from 30% to 70% of the total heat capacity of calorimetric ampoule + substance over the range between 7 and 630 K. The averaging of the experimental C_p° points in the region with no transformations was made in the form of degree and semilogarithmic polynomials, the corresponding coefficients were chosen by means of computer programs. So, for example, the following equations were used:

$$C_p^{\circ} = 9.6423 - 40.02 \left(\frac{T}{30}\right) + 122.76 \left(\frac{T}{30}\right)^2$$
$$-97.599 \left(\frac{T}{30}\right)^3 + 38.865 \left(\frac{T}{30}\right)^4 - 7.6606 \left(\frac{T}{30}\right)^5$$
$$+ 0.59495 \left(\frac{T}{30}\right)^6$$

in the range from T = (25 to 100) K;

$$C_p^{\circ} = -1.312792 \times 10^5 + 4.167009 \times 10^5 \ln\left(\frac{T}{30}\right)$$
$$-5.488911 \times 10^5 \ln^2\left(\frac{T}{30}\right) + 3.842331 \times 10^5 \ln^3$$
$$\times \left(\frac{T}{30}\right) - 1.507253 \times 10^5 \ln^4\left(\frac{T}{30}\right) + 3.141533$$
$$\times 10^4 \ln^5\left(\frac{T}{30}\right) - 2.718069 \times 10^3 \ln^6\left(\frac{T}{30}\right)$$

in the range from T = (150 to 250) K.

In the above equations the C_p° is given in J K⁻¹ mol⁻¹ and T in Kelvin degree.



Fig. 3. Temperature dependence of heat capacity of CsTaWO₆.

Their root mean square deviation from the averaging $C_p^{\circ} = f(T)$ curve was $\pm 0.15\%$ in the range T = (6-40) K, $\pm 0.075\%$ from T = (40 to 80) K, $\pm 0.050\%$ between T = (80 and 350) K and $\pm 0.5\%$ over the range from T = (350 to 630) K.

The experimental values of the molar heat capacity of CsTaWO₆ over the range from 7 to 630 K and the averaging $C_p^{\circ} = f(T)$ plot are presented in Fig. 3. The heat capacity C_p° of this substance gradually increases with rising temperature and does not show any peculiarities until 630 K.

3.3. Standard thermodynamic functions

To calculate the standard thermodynamic functions (Table 3) of the cesium tantalum tungsten oxide, its C_p° values were extrapolated from the temperature of the measurement beginning at approximately 7–0 K by Debye's function of heat capacity:

$$C_p^{\circ} = nD\left(\frac{\theta_{\rm D}}{T}\right),\tag{1}$$

where *D* is the symbol of Debye's function, n=5 and $\theta_D = 100.6$ K are specially selected parameters. Eq. (1) with the above parameters describes the experimental C_p° values of the compound between 7 and 12 K with the error of $\pm 1.0\%$. In calculating the functions it was assumed that Eq. (1) reproduces the C_p° values of CsTaWO₆ at T < 7 K with the same error. The calculations of $H^{\circ}(T) - H^{\circ}(0)$ and $S^{\circ}(T) - S^{\circ}(0)$ were made by the numerical integration of $C_p^{\circ} = f(T)$ and $C_p^{\circ} = f(\ln T)$ curves, respectively, and the Gibbs function $G^{\circ}(T) - H^{\circ}(0)$ was estimated from the enthalpies and entropies at the corresponding temperatures [19]. It was suggested that the error of the function values was $\pm 1\%$ at T < 40 K, $\pm 0.5\%$ between 40 and 80 K, $\pm 0.2\%$ in the range from 80 to 350 K and $\pm 1.5\%$ between 350 and 630 K.

The absolute entropies of cesium tantalum tungsten oxide (Table 3) and the corresponding simple substances W(cr), Ta (cr), Cs (cr) [20] and O₂ (g) [21] were used to

Table 3
Thermodynamic functions of crystalline CsTaWO ₆ ; $M = 593.6997 \text{ g mol}^{-1}$, $p^{\circ} = 0.1 \text{ MPa}$

0 0 0 0 0 5 0.250 0.0000290 0.0566 0.000024 10 3.11 0.000777 0.901 0.00115 20 15.16 0.09544 6.543 0.03543 25 21.07 0.1863 10.57 0.07808 30 26.65 0.3956 1.491 0.1417 35 32.05 0.4525 2.404 0.3361 40 37.03 0.6225 2.404 0.3361 50 4.676 1.043 3332 0.6228 55 50.56 1.287 37.96 0.8011 60 54.64 1.550 4.253 1.002 65 58.69 1.833 47.06 1.226 70 62.86 2.137 51.56 1.473 75 67.11 2.462 56.05 1.742 80 71.33 2.898 60.51 2.268 100 87.27 4.397	T (K)	$C_p^{\circ}(T) (\mathrm{J}\mathrm{K}^{-1}\mathrm{mol}^{-1})$	$H^{\circ}(T) - H^{0}(0) (\text{kJ mol}^{-1})$	$S^{\circ}(T) (\mathrm{J}\mathrm{K}^{-1}\mathrm{mol}^{-1})$	$-[\mathbf{G}^{\circ}(T) - H^{\circ}(0)] (\mathrm{kJ}\mathrm{mol}^{-1})$
50.2500.0002900.05660.00193103.110.001770.0010.00193158.690.05583.160.01543252.1070.186310.570.07808260.30561.4910.277532.02.6650.452524.640.22754037.030.625524.640.4679554.620.821928.660.6228565.561.28737.060.6216575.561.28737.060.6228585.562.1375.1561.4737567.112.46256051.7427567.112.46256051.7427567.112.46295362.4347567.112.46295362.434767.1333.56296.351.577109.4515.36686.844.2467109.4515.3661.6317101.529.601119.98.9007101.541.591.577101.541.531.557101.541.521.537101.541.531.557101.541.541.557101.541.591.577101.541.591.577101.541.591.577101.541.591.577111.541.591.55 <trr< td=""><td>0</td><td>0</td><td>0</td><td>0</td><td>0</td></trr<>	0	0	0	0	0
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158.090.05883.160.01512015.160.005446.5430.03532521.070.186310.570.078083026.650.305614.910.14173532.050.452524.040.33614541.620.821928.660.46795044.761.04333.220.62285550.561.28737.960.80116658.691.83347.061.2266767.112.46256.051.7427567.112.46256.051.742807.332.56269.392.6839079.533.56269.392.68310084.515.30686.844.24611094.515.30686.844.24612010.59.601119.98.3901601.471.62215.51.6951701.5.51.6951.571.551801.34.71.34.21.311.341901.35.41.62015.88.6921901.35.41.62015.81.6961901.552.0401.584.621901.341.62015.81.6961901.552.0402.712.662.8721901.541.921.8542.2221801.47.91.653.693.611901.57.72.66	10	3.11	0.00707	0.901	0.00193
2015.160.095446.5.430.037332521.070.186310.570.078083026.650.305614.4910.14173532.050.452519.430.32164037.030.625524.040.33015047.661.04333.320.62285150.561.28737.960.80116254.641.55042.351.0026555.661.28737.961.2267062.862.13751.561.7428071.332.80860.511.7429073.533.56269.392.6839073.533.56269.392.68311094.515.30686.844.246120101.36.28695.361.517130107.67.330103.776.15315019.39.60111.998.39015019.39.60111.998.30217012.812.09135.510.9518013.4714.79150.513.8119013.4414.79150.513.8119013.4414.79150.513.8119013.4414.79150.513.8120114.782.2222.22220215.520.7017.872.46620315.520.7017.872.46620415.952.6722.	15	8.69	0.0358	3.16	0.0115
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40 7.03 0.6255 24.04 0.3361 55 4.676 1.043 33.52 0.6228 55 50.56 1.287 37.96 0.8011 65 58.69 1.833 47.06 1.226 67 62.86 2.137 51.56 1.473 75 67.11 2.462 56.05 1.742 80 71.33 2.808 60.51 2.033 90 79.53 3.562 69.39 2.683 100 87.27 4.397 78.18 3.421 120 101.3 6.286 95.36 5.157 130 107.6 7.330 105.7 6.153 140 113.6 8.437 111.9 7.231 150 124.7 10.82 127.8 9.629 160 124.7 10.82 127.8 9.629 170 129.8 1200 135.5 10.05 180 14.37 15.4<	35	32.05	0.4525	19.43	0.2275
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60 54.64 1.550 42.33 1.002 65 58.69 1.833 47.06 1.226 70 62.86 2.137 51.56 1.742 75 67.11 2.462 56.05 1.742 80 71.33 2.808 60.51 2.033 90 79.53 3.562 69.39 2.683 100 87.27 4.397 78.18 3.421 110 94.51 5.306 86.84 4.246 120 101.3 6.286 95.36 5.157 130 107.6 7.330 103.7 6.153 140 113.6 8.437 111.9 7.231 150 19.3 9.001 119.9 8.390 160 124.7 10.82 127.8 9.629 170 129.8 12.00 135.5 10.95 180 13.47 13.42 143.1 12.34 190 139.4 14.79 150.5 13.81 200 143.8 16.20 17.8 13.55 210 147.9 17.66 164.9 16.96 220 155.5 20.70 178.7 20.40 240 159.6 27.18 20.40 24.11 260 165.2 25.52 198.4 26.06 27.11 20.66 28.72 29.8 34.93 300 175.7 32.24 22.86 34.49 300 175.7 32.4	55	50.56	1.287	37.96	0.8011
65 88.69 1.833 47.06 1.226 70 62.86 2.137 51.56 1.473 80 71.33 2.808 60.51 2.033 90 79.53 3.562 69.39 2.683 100 87.27 4.397 78.18 3.421 110 94.51 5.306 86.84 4.246 120 10.3 6.286 95.36 5.157 130 107.6 7.330 103.7 6.153 140 113.6 8.377 111.9 7.231 150 119.3 9.601 119.9 8.390 160 124.7 10.82 127.8 9.629 170 129.8 12.09 135.5 10.95 180 134.7 13.42 143.1 12.34 200 143.8 16.20 157.8 15.35 210 147.9 17.66 164.9 16.96 220 151.9 19.16 171.9 18.65 230 155.5 20.70 178.7 20.40 240 190.0 22.27 188.4 22.22 250 162.2 25.52 198.4 26.06 270 168.0 27.18 20.66 28.77 280 170.7 28.87 210.8 30.15 290 173.3 30.59 21.68 32.29 281.5 175.7 32.34 22.86 36.74 300 175.7 32.34 22.86 36.74 <td>60</td> <td>54 64</td> <td>1 550</td> <td>42.53</td> <td>1.002</td>	60	54 64	1 550	42.53	1.002
70 62.86 2.137 51.56 1.473 75 67.11 2.462 56.05 1.742 80 71.33 2.808 60.51 2.033 90 79.53 3.562 69.39 2.683 100 87.27 4.397 78.18 3.421 110 94.51 5.306 86.84 4.246 120 101.3 6.286 95.36 5.157 130 107.6 7.330 103.7 6.153 140 113.6 8.437 111.9 7.231 150 19.3 9.601 119.9 8.390 160 124.7 10.82 127.8 9.629 170 128.8 12.09 135.5 10.95 180 134.7 13.42 143.1 12.34 190 139.4 14.79 150.5 13.81 200 143.8 16.20 157.8 15.35 210 147.9 17.66 164.9 16.96 220 151.9 9.166 71.9 8.65 230 155.5 20.70 78.7 20.40 240 159.0 22.27 185.4 22.22 2552 198.4 26.06 28.77 273.15 168.9 27.71 206.6 28.72 280 170.7 28.87 210.8 30.15 290 173.3 35.09 216.8 32.29 291.5 175.3 32.02	65	58 69	1 833	47.06	1 226
73 67.11 2.462 56.05 1.742 80 71.33 2.808 60.51 2.033 90 79.53 3.562 69.39 2.683 100 87.27 4.397 78.18 3.421 110 94.51 5.306 86.84 4.246 120 101.3 6.286 95.36 5.157 130 107.6 7.330 103.7 6.153 140 113.6 8.437 111.9 7.231 150 119.3 9.601 119.9 8.390 160 124.7 10.82 127.8 9.629 170 129.8 12.09 135.5 10.95 180 134.7 13.42 143.11 12.34 190 139.4 14.79 150.5 13.81 200 143.8 16.20 171.9 18.65 210 147.9 17.66 164.9 16.96 220 151.9 19.16 171.9 18.65 230 155.5 20.70 178.7 20.40 240 159.0 22.27 185.4 22.22 250 162.2 25.52 198.4 26.06 270 168.0 27.18 20.46 28.07 273.15 68.0 27.18 24.11 22.29 280 170.7 28.87 210.8 30.15 290 175.3 30.29 24.8 34.49 300 175.7 <td< td=""><td>70</td><td>62.86</td><td>2 137</td><td>51 56</td><td>1 473</td></td<>	70	62.86	2 137	51 56	1 473
10 $1,142$ $2,002$ $1,142$ 90 $79,53$ $3,562$ $69,39$ $2,683$ 100 $87,27$ $4,397$ $78,18$ $3,421$ 110 $94,51$ $5,306$ $86,84$ $4,246$ 120 $101,3$ $6,286$ $95,36$ $5,157$ 130 $107,6$ $7,330$ $103,7$ $6,153$ 140 $113,6$ $8,437$ $111,9$ $7,231$ 150 $19,3$ $9,601$ $119,9$ $8,390$ 160 $124,7$ $10,82$ $127,8$ $9,629$ 170 $129,8$ $12,09$ $135,5$ $10,95$ 180 $134,7$ $13,42$ $143,1$ $12,34$ 190 $139,4$ $14,79$ $150,5$ $13,81$ 200 $143,8$ $16,20$ $157,8$ $15,35$ 210 $147,9$ $17,66$ $164,9$ $6,966$ 220 $151,9$ $19,16$ $171,9$ $18,65$ 230 $155,5$ $20,70$ $178,7$ $20,40$ 240 $159,0$ $22,27$ $185,4$ $22,22$ 250 $162,2$ $25,52$ $198,4$ $26,06$ 270 $168,0$ $27,18$ $20,66$ $28,72$ 280 $170,7$ $22,87$ $216,8$ $30,15$ 290 $173,3$ $30,59$ $216,8$ $32,29$ $298,15$ $175,3$ $32,02$ $221,7$ $34,08$ 300 $175,7$ $32,34$ $228,6$ $36,74$ 300 $175,7$ $32,34$ <t< td=""><td>75</td><td>67.11</td><td>2.157</td><td>56.05</td><td>1 742</td></t<>	75	67.11	2.157	56.05	1 742
30 79.53 2.603 3.562 69.39 2.683 100 87.27 4.397 78.18 3.421 110 94.51 5.306 86.84 4.246 120 101.3 6.286 95.36 5.157 130 107.6 7.330 103.7 6.153 140 113.6 8.437 111.9 7.231 150 119.3 9.601 119.9 8.390 160 124.7 10.82 127.8 9.629 170 129.8 12.09 135.5 10.95 180 134.7 13.42 143.1 2.234 200 143.8 16.20 157.8 15.35 210 147.9 17.66 164.9 16.96 220 151.9 19.16 171.9 18.65 230 155.5 20.70 178.7 20.40 240 159.0 22.27 188.4 20.606 27.18 25.52 198.4 26.06 270 168.9 27.71 206.6 28.72 280 170.7 28.87 210.8 30.15 290 173.3 30.59 216.8 32.29 28.15 175.3 32.02 221.7 34.08 300 175.7 32.34 222.8 34.49 310 178.2 34.11 228.6 36.74 320 180.6 35.90 234.3 39.06 330 183.1 <td>80</td> <td>71 33</td> <td>2.402</td> <td>60.51</td> <td>2 033</td>	80	71 33	2.402	60.51	2 033
30 12.3 35.32 0.93 2.483 100 87.27 4.397 78.18 3.421 110 94.51 5.306 86.84 4.246 120 101.3 6.286 95.36 5.157 130 107.6 7.330 103.7 6.153 140 113.6 8.437 111.9 7.231 150 119.3 9.601 119.9 8.390 160 124.7 10.82 127.8 9.629 170 129.8 12.09 135.5 10.95 180 134.7 13.42 143.1 12.34 190 139.4 14.79 150.5 13.81 200 143.8 16.20 157.8 15.35 210 147.9 17.66 164.9 16.96 220 155.5 20.70 178.7 20.40 240 159.0 22.77 185.4 22.22 250 162.2 23	90	70.53	3 562	60.30	2.655
100 30.21 4.397 10.18 3.421 110 94.51 5.306 86.84 4.246 120 101.3 6.286 95.36 5.157 130 107.6 7.330 103.7 6.153 140 113.6 8.437 111.9 7.231 150 119.3 9.601 119.9 8.390 160 124.7 10.82 127.8 9.629 170 129.8 12.09 135.5 10.95 180 134.7 13.42 143.1 12.34 190 139.4 14.79 150.5 13.81 200 143.8 16.20 157.8 15.35 210 147.9 17.66 164.9 16.96 220 151.9 19.16 171.9 18.65 230 155.5 20.70 178.7 20.40 240 159.0 22.77 188.4 22.22 250 162.2 23.88 191.9 24.11 260 165.2 25.52 198.4 26.06 270 188.0 27.18 24.06 28.07 271.1 20.66 28.72 29.81 32.49 280 170.7 28.87 210.8 32.29 281.5 175.3 32.02 216.8 32.29 284.5 175.7 32.34 228.6 36.74 300 175.7 32.34 228.6 36.74 301 178.2 34.11 228.6 36.74 <	100	79.35 87 07	4 307	78.18	2.005
110 $3-3.0$ 3.00 30.04 $4-2.40$ 120101.3 6.286 95.36 51.57 130107.6 7.330 103.7 6.153 140113.6 8.437 111.9 7.231 150119.3 9.601 119.9 8.390 160124.710.82127.8 9.629 170129.812.09135.510.95180134.713.42143.112.34190139.414.79150.513.81200143.816.20157.815.35210147.917.66164.916.96220151.919.16171.918.65230155.520.70178.720.40240159.022.27185.422.22250162.223.88191.924.11260165.225.52198.426.06273.15168.927.71206.628.72280170.728.87210.830.15290173.330.59216.832.29298.15175.332.0221.734.08300175.732.3422.8636.74320180.635.90234.339.06330183.137.72239.841.43340185.839.57245.443.85350188.641.44250.846.33340213.161.5730.1373.99 <t< td=""><td>110</td><td>04.51</td><td>5 206</td><td>26.24</td><td>4.246</td></t<>	110	04.51	5 206	26.24	4.246
120101.310.280 $9.5.0$ 51.0 51.0 130107.67.330103.7 6.153 140113.6 8.437 111.9 7.231 150119.39.601119.9 8.390 160124.710.82127.8 9.629 170129.812.09135.510.95180134.713.42143.112.34190139.414.79150.513.81200143.816.20157.815.35210147.917.66164.916.96220151.919.16171.918.65230155.520.70178.720.40240159.022.27185.422.22250162.223.88191.924.11260165.225.52198.426.06270168.927.18204.628.07273.15168.927.7120.6628.72280170.728.87210.830.15290173.330.59216.832.29281.5175.332.0222.1734.08300175.732.3422.834.49310178.234.11228.636.74320180.635.90234.339.06330183.137.72239.841.43340185.839.57245.443.85350188.641.44250.846.33 <t< td=""><td>110</td><td>94.51 101.2</td><td>5.300</td><td>05 26</td><td>4.240</td></t<>	110	94.51 101.2	5.300	05 26	4.240
13010.01.35010.0.70.13140113.68.437111.97.231150119.39.601119.98.390160124.710.82127.89.629170129.812.09135.510.95180134.713.42143.112.34190139.414.79150.513.81200143.816.20157.815.35210147.917.66164.916.96220151.919.16171.918.65230155.520.70178.720.40240159.022.27185.422.22250162.223.88191.924.11260165.225.52198.426.06270168.027.18204.628.07273.15168.927.7120.6628.72280170.728.87210.830.15290173.330.59216.832.29281.5175.332.02221.734.08300175.732.34222.834.49310178.234.11228.636.74320180.635.90234.339.06330183.137.72239.841.43340185.839.57245.443.85350188.641.44250.846.334400201.651.20276.859.53350235.4	120	107.6	7 220	102.7	6 152
140 113.0 8.437 111.9 1.231 150 119.3 9.601 119.9 8.390 160 124.7 10.82 127.8 9.629 170 129.8 12.09 135.5 10.95 180 134.7 13.42 143.1 12.34 190 139.4 14.79 150.5 13.81 200 143.8 16.20 157.8 15.35 210 147.9 17.66 164.9 16.96 220 151.9 19.16 171.9 18.65 230 155.5 20.70 178.7 20.40 240 159.0 22.27 185.4 22.22 250 162.2 23.88 191.9 24.11 260 165.2 25.52 198.4 26.06 270 168.0 27.71 20.66 28.72 280 170.7 28.87 210.8 30.15 290 173.3 30.59 216.8 32.29 28.15 175.3 32.02	130	107.0	7.330 9.427	103.7	0.155
130 19.5 9.001 119.5 8.390 160 124.7 10.82 127.8 9.629 170 129.8 12.09 135.5 10.95 180 134.7 13.42 143.1 12.34 200 143.8 16.20 157.8 15.35 210 147.9 17.66 164.9 16.96 220 151.9 19.16 171.9 18.65 230 155.5 20.70 178.7 20.40 240 159.0 22.27 185.4 22.22 250 162.2 23.88 191.9 24.11 260 165.2 25.52 198.4 26.06 270.1 168.0 27.18 204.6 28.07 273.15 168.9 27.71 206.6 28.72 280 170.7 28.87 210.8 30.15 290 173.3 30.59 216.8 32.29 28.15 175.3	140	115.0	0.437	111.9	200
100 124.7 10.82 12.78 30.29 170 129.8 12.09 135.5 10.095 180 134.7 13.42 143.1 12.34 190 139.4 14.79 150.5 13.81 200 143.8 1620 157.8 15.35 210 147.9 17.66 164.9 16.96 220 151.9 19.16 171.9 18.65 230 155.5 20.70 178.7 20.40 240 159.0 22.27 185.4 22.22 250 162.2 23.88 191.9 24.11 260 165.2 25.52 198.4 26.06 270 168.0 27.18 204.6 28.07 273.15 168.9 27.71 206.6 28.72 280 170.7 28.87 210.8 30.15 290 173.3 30.59 216.8 32.29 298.15 175.3 32.02 221.7 34.08 300 175.7 32.34 222.8 34.49 310 178.2 34.11 228.6 36.74 320 180.6 35.90 234.3 39.06 330 183.1 37.72 29.8 41.43 340 185.8 39.57 245.4 43.85 350 18.6 41.44 250.8 46.33 400 201.6 51.20 276.8 59.53 550 235.4 <td>150</td> <td>119.3</td> <td>9.001</td> <td>119.9</td> <td>8.390</td>	150	119.3	9.001	119.9	8.390
170 129.8 12.09 135.5 10.95 180 134.7 13.42 143.1 12.34 190 139.4 14.79 150.5 13.81 200 143.8 16.20 157.8 15.35 210 147.9 17.66 164.9 16.96 220 151.9 19.16 171.9 18.65 230 155.5 20.70 178.7 20.40 240 159.0 22.27 185.4 22.22 250 162.2 23.88 191.9 24.11 260 165.2 25.52 198.4 26.06 273.15 168.9 27.18 204.6 28.07 273.15 168.9 27.71 206.6 28.72 280 170.7 28.87 210.8 30.15 290 173.3 30.59 216.8 32.29 298.15 175.3 32.02 221.7 34.08 300 175.7 32.34 222.8 34.49 310 178.2 34.11 228.6 36.74 320 180.6 35.90 234.3 39.06 330 183.1 37.72 239.8 41.43 340 185.8 39.57 245.4 43.85 350 188.6 41.44 250.8 46.33 400 201.6 51.20 276.8 59.53 550 235.4 84.00 346.2 106.4 600 24.5	160	124.7	10.82	127.8	9.629
180 134.7 13.42 14.51 12.34 190 139.4 14.79 150.5 13.81 200 143.8 16.20 157.8 15.35 210 147.9 17.66 164.9 16.96 220 151.9 19.16 171.9 18.65 230 155.5 20.70 178.7 20.40 240 159.0 22.27 185.4 22.22 250 162.2 23.88 191.9 24.11 260 165.2 25.52 198.4 26.06 270 188.0 27.18 204.6 28.07 273.15 168.9 27.71 206.6 28.72 280 170.7 28.87 210.8 30.15 290 173.3 30.59 216.8 32.29 281.5 175.3 32.02 221.7 34.08 300 175.7 32.34 222.8 34.49 310 178.2 34.11 228.6 36.74 320 180.6 35.90 234.3 39.06 330 183.1 37.72 239.8 41.43 340 185.8 39.57 245.4 43.85 350 188.6 41.44 250.8 46.33 400 201.6 51.20 276.8 59.53 550 235.4 84.00 346.2 106.4 650 249.2 103.4 379.2 135.4	170	129.8	12.09	135.5	10.95
190139.414.79150.515.81200143.816.20157.815.35210147.917.66164.916.96220151.919.16171.918.65230155.520.70178.720.40240159.022.27185.422.22250162.223.88191.924.11260165.225.52198.426.06270168.927.71206.628.72280170.728.87210.830.15290173.330.59216.832.29298.15175.332.02221.734.08300175.732.34222.834.49310178.234.11228.636.74330183.137.72239.841.43340185.839.57245.443.85350188.641.44250.846.33400201.651.20276.859.53550235.484.00366.2106.460024.372.51324.389.63550235.484.00367.1124.2630249.2103.4379.2135.4	180	134./	13.42	143.1	12.34
200 143.8 16.20 157.8 15.55 210 147.9 17.66 164.9 16.96 220 151.9 19.16 171.9 18.65 230 155.5 20.70 178.7 20.40 240 159.0 22.27 185.4 22.22 250 162.2 23.88 191.9 24.11 260 165.2 25.52 198.4 26.06 270 168.0 27.18 204.6 28.07 273.15 168.9 27.71 206.6 28.72 280 170.7 28.87 210.8 30.15 290 173.3 30.59 216.8 32.29 298.15 175.7 32.34 222.8 34.49 300 178.7 32.34 228.6 36.74 320 180.6 35.90 234.3 39.06 330 183.1 37.72 239.8 41.43 340 185.8 39	190	139.4	14.79	150.5	13.81
210 $14/.9$ 17.66 164.9 16.96 220 151.9 19.16 171.9 18.65 230 155.5 20.70 178.7 20.40 240 159.0 22.27 185.4 22.22 250 162.2 23.88 191.9 24.11 260 165.2 25.52 198.4 26.06 270 168.0 27.18 204.6 28.07 273.15 168.9 27.71 206.6 28.72 280 170.7 28.87 210.8 30.15 290 173.3 30.59 216.8 32.29 28.15 175.3 32.02 221.7 34.08 300 175.7 32.34 222.8 34.49 310 178.2 34.11 228.6 36.74 320 180.6 35.90 234.3 39.06 330 183.1 37.72 239.8 41.43 340 185.8 39.57 245.4 43.85 350 18.6 41.44 250.8 46.33 400 201.6 51.20 276.8 59.53 550 234.3 72.51 324.3 89.63 550 235.4 84.00 346.2 106.4 600 249.2 103.4 379.2 135.4	200	143.8	16.20	157.8	15.35
220 151.9 19.16 171.9 18.65 230 155.5 20.70 178.7 20.40 240 159.0 22.27 185.4 22.22 250 162.2 23.88 191.9 24.11 260 165.2 25.52 198.4 26.06 270 168.0 27.18 204.6 28.07 273.15 168.9 27.71 206.6 28.72 280 170.7 28.87 210.8 30.15 290 173.3 30.59 216.8 32.29 298.15 175.3 32.02 221.7 34.08 300 175.7 32.34 222.8 34.49 310 178.2 34.11 228.6 36.74 320 180.6 35.90 234.3 39.06 330 183.1 37.72 239.8 41.43 340 185.8 39.57 245.4 43.85 350 188.6 41.44 250.8 46.33 400 201.6 51.20 276.8 59.53 450 213.1 61.57 301.3 73.99 500 224.3 72.51 324.3 89.63 550 235.4 84.00 346.2 106.4 600 245.1 96.03 367.1 124.2 630 249.2 103.4 379.2 135.4	210	147.9	17.66	164.9	16.96
230 155.5 20.70 178.7 20.40 240 159.0 22.27 185.4 22.22 250 162.2 23.88 191.9 24.11 260 165.2 25.52 198.4 26.06 270 168.0 27.18 204.6 28.07 273.15 168.9 27.71 206.6 28.72 280 170.7 28.87 210.8 30.15 290 173.3 30.59 216.8 32.29 298.15 175.3 32.02 221.7 34.08 300 175.7 32.34 222.8 34.49 310 178.2 34.11 228.6 36.74 320 180.6 35.90 234.3 39.06 330 183.1 37.72 239.8 41.43 340 185.8 39.57 245.4 43.85 350 188.6 41.44 250.8 46.33 400 201.6 51.20 276.8 59.53 450 213.1 61.57 301.3 73.99 500 224.3 72.51 324.3 89.63 550 235.4 84.00 346.2 106.4 600 245.1 96.03 367.1 124.2 630 249.2 103.4 379.2 135.4	220	151.9	19.16	171.9	18.65
240 159.0 22.27 185.4 22.22 250 162.2 23.88 191.9 24.11 260 165.2 25.52 198.4 26.06 270 168.0 27.18 204.6 28.07 273.15 168.9 27.71 206.6 28.72 280 170.7 28.87 210.8 30.15 290 173.3 30.59 216.8 32.29 298.15 175.7 32.34 222.8 34.49 310 178.2 34.11 228.6 36.74 320 180.6 35.90 234.3 39.06 330 183.1 37.72 239.8 41.43 340 185.8 39.57 245.4 43.85 350 188.6 41.44 250.8 46.33 400 201.6 51.20 276.8 59.53 450 213.1 61.57 301.3 73.99 500 224.3 72.51 324.3 89.63 550 235.4 84.00 346.2 106.4 600 245.1 96.03 367.1 124.2 630 249.2 103.4 379.2 135.4	230	155.5	20.70	178.7	20.40
250 162.2 23.88 191.9 24.11 260 165.2 25.52 198.4 26.06 270 168.0 27.18 204.6 28.07 273.15 168.9 27.71 206.6 28.72 280 170.7 28.87 210.8 30.15 290 173.3 30.59 216.8 32.29 298.15 175.3 32.02 221.7 34.08 300 175.7 32.34 222.8 34.49 310 178.2 34.11 228.6 36.74 320 180.6 35.90 234.3 39.06 330 183.1 37.72 239.8 41.43 340 185.8 39.57 245.4 43.85 550 213.1 61.57 301.3 73.99 500 224.3 72.51 324.3 89.63 550 235.4 84.00 346.2 106.4 600 245.1 96.03 37.2 135.4	240	159.0	22.27	185.4	22.22
260 165.2 25.52 198.4 26.06 270 168.0 27.18 204.6 28.07 273.15 168.9 27.71 206.6 28.72 280 170.7 28.87 210.8 30.15 290 173.3 30.59 216.8 32.29 298.15 175.3 32.02 221.7 34.08 300 175.7 32.34 222.8 34.49 310 178.2 34.11 228.6 36.74 320 180.6 35.90 234.3 39.06 330 183.1 37.72 239.8 41.43 340 185.8 39.57 245.4 43.85 350 188.6 41.44 250.8 46.33 400 201.6 51.20 276.8 59.53 550 223.4 72.51 324.3 89.63 550 235.4 84.00 346.2 106.4 600 245.1 96.03 367.1 124.2 630 249.2 103.4 379.2 135.4	250	162.2	23.88	191.9	24.11
270 168.0 27.18 204.6 28.07 273.15 168.9 27.71 206.6 28.72 280 170.7 28.87 210.8 30.15 290 173.3 30.59 216.8 32.29 298.15 175.3 32.02 221.7 34.08 300 175.7 23.34 222.8 34.49 310 178.2 34.11 228.6 36.74 320 180.6 35.90 234.3 39.06 330 183.1 37.72 239.8 41.43 340 185.8 39.57 245.4 43.85 350 188.6 41.44 250.8 46.33 400 201.6 51.20 276.8 59.53 550 235.4 84.00 346.2 106.4 600 245.1 96.03 367.1 124.2 630 249.2 103.4 379.2 135.4	260	165.2	25.52	198.4	26.06
273.15 168.9 27.71 206.6 28.72 280 170.7 28.87 210.8 30.15 290 173.3 30.59 216.8 32.29 298.15 175.3 32.02 221.7 34.08 300 175.7 32.34 222.8 34.49 310 178.2 34.11 228.6 36.74 320 180.6 35.90 234.3 39.06 330 183.1 37.72 239.8 41.43 340 185.8 39.57 245.4 43.85 350 188.6 41.44 250.8 46.33 450 213.1 61.57 301.3 73.99 500 224.3 72.51 324.3 89.63 550 235.4 84.00 367.1 124.2 630 249.2 103.4 379.2 135.4	270	168.0	27.18	204.6	28.07
280 170.7 28.87 210.8 30.15 290 173.3 30.59 216.8 32.29 298.15 175.3 32.02 221.7 34.08 300 175.7 32.34 222.8 34.49 310 178.2 34.11 228.6 36.74 320 180.6 35.90 234.3 39.06 330 183.1 37.72 239.8 41.43 340 185.8 39.57 245.4 43.85 350 188.6 41.44 250.8 46.33 400 201.6 51.20 276.8 59.53 500 224.3 72.51 224.3 89.63 550 235.4 84.00 346.2 106.4 600 245.1 96.03 367.1 124.2 630 249.2 103.4 379.2 135.4	273.15	168.9	27.71	206.6	28.72
290 173.3 30.59 216.8 32.29 298.15 175.3 32.02 221.7 34.08 300 175.7 32.34 222.8 34.49 310 178.2 34.11 228.6 36.74 320 180.6 35.90 234.3 39.06 330 183.1 37.72 239.8 41.43 340 185.8 39.57 245.4 43.85 350 188.6 41.44 250.8 46.33 400 201.6 51.20 276.8 59.53 450 213.1 61.57 301.3 73.99 500 224.3 72.51 324.3 89.63 550 235.4 84.00 346.2 106.4 600 245.1 96.03 367.1 124.2 630 249.2 103.4 379.2 135.4	280	170.7	28.87	210.8	30.15
298.15 175.3 32.02 221.7 34.08 300 175.7 32.34 222.8 34.49 310 178.2 34.11 228.6 36.74 320 180.6 35.90 234.3 39.06 330 183.1 37.72 239.8 41.43 340 185.8 39.57 245.4 43.85 350 188.6 41.44 250.8 46.33 400 201.6 51.20 276.8 59.53 450 213.1 61.57 301.3 73.99 500 224.3 72.51 324.3 89.63 550 235.4 84.00 346.2 106.4 600 245.1 96.03 367.1 124.2 630 249.2 103.4 379.2 135.4	290	173.3	30.59	216.8	32.29
300 175.7 32.34 222.8 34.49 310 178.2 34.11 228.6 36.74 320 180.6 35.90 234.3 39.06 330 183.1 37.72 239.8 41.43 340 185.8 39.57 245.4 43.85 350 188.6 41.44 250.8 46.33 400 201.6 51.20 276.8 59.53 450 213.1 61.57 301.3 73.99 500 224.3 72.51 324.3 89.63 550 235.4 84.00 346.2 106.4 600 245.1 96.03 367.1 124.2 630 249.2 103.4 379.2 135.4	298.15	175.3	32.02	221.7	34.08
310 178.2 34.11 228.6 36.74 320 180.6 35.90 234.3 39.06 330 183.1 37.72 239.8 41.43 340 185.8 39.57 245.4 43.85 350 188.6 41.44 250.8 46.33 400 201.6 51.20 276.8 59.53 450 213.1 61.57 301.3 73.99 500 224.3 72.51 324.3 89.63 550 235.4 84.00 346.2 106.4 600 245.1 96.03 367.1 124.2 630 249.2 103.4 379.2 135.4	300	175.7	32.34	222.8	34.49
320 180.6 35.90 234.3 39.06 330 183.1 37.72 239.8 41.43 340 185.8 39.57 245.4 43.85 350 188.6 41.44 250.8 46.33 400 201.6 51.20 276.8 59.53 450 213.1 61.57 301.3 73.99 500 224.3 72.51 324.3 89.63 550 235.4 84.00 346.2 106.4 600 245.1 96.03 367.1 124.2 630 249.2 103.4 379.2 135.4	310	178.2	34.11	228.6	36.74
330 183.1 37.72 239.8 41.43 340 185.8 39.57 245.4 43.85 350 188.6 41.44 250.8 46.33 400 201.6 51.20 276.8 59.53 450 213.1 61.57 301.3 73.99 500 224.3 72.51 324.3 89.63 550 235.4 84.00 346.2 106.4 600 245.1 96.03 367.1 124.2 630 249.2 103.4 379.2 135.4	320	180.6	35.90	234.3	39.06
340185.839.57245.443.85350188.641.44250.846.33400201.651.20276.859.53450213.161.57301.373.99500224.372.51324.389.63550235.484.00346.2106.4600245.196.03367.1124.2630249.2103.4379.2135.4	330	183.1	37.72	239.8	41.43
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	340	185.8	39.57	245.4	43.85
400201.651.20276.859.53450213.161.57301.373.99500224.372.51324.389.63550235.484.00346.2106.4600245.196.03367.1124.2630249.2103.4379.2135.4	350	188.6	41.44	250.8	46.33
450213.161.57301.373.99500224.372.51324.389.63550235.484.00346.2106.4600245.196.03367.1124.2630249.2103.4379.2135.4	400	201.6	51.20	276.8	59.53
500224.372.51324.389.63550235.484.00346.2106.4600245.196.03367.1124.2630249.2103.4379.2135.4	450	213.1	61.57	301.3	73.99
550235.484.00346.2106.4600245.196.03367.1124.2630249.2103.4379.2135.4	500	224.3	72.51	324.3	89.63
600245.196.03367.1124.2630249.2103.4379.2135.4	550	235.4	84.00	346.2	106.4
630 249.2 103.4 379.2 135.4	600	245.1	96.03	367.1	124.2
	630	249.2	103.4	379.2	135.4

calculate the standard entropy of formation of the compound under study at 298.15 K, $\Delta_f S^{\circ}(298.15, \text{ CsTaWO}_6, \text{ cr}) = -553.2 \pm 2.1 \text{ J K}^{-1} \text{ mol}^{-1}$.

mial:

$$a = 1.68 \cdot 10^{-8} \cdot T^2 + 3.89 \cdot 10^{-5} \cdot T + 10.3681(298 \le T) \le 1073 \text{ K}.$$
(2)

3.4. High-temperature X-ray diffraction

The dependence of the unit cell parameter is plotted in Fig. 4 and Table 4, and it is described by the following square polyno-

The average thermal expansion coefficient $\alpha_{av} = 5.92 \times 10^{-6} \text{ K}^{-1}$ obtained for the cesium tantalum



Fig. 4. Plot of unit cell parameter vs. temperature for CsTaWO₆.

Table 4 Parameters of unit cells and thermal expansion coefficients vs. temperature for CsTaWO₆

<i>T</i> (K)	a (Å)	$V(Å^3)$	$\rho({\rm gcm^{-3}})$	$\alpha (\times 10^6 \mathrm{K}^{-1})$
298	10.3793(2)	1118.14(4)	7.051	4.71
373	10.3865(9)	1120.5(3)	7.036	4.95
473	10.3917(8)	1122.2(3)	7.026	5.27
573	10.3958(8)	1123.5(3)	7.018	5.59
673	10.4025(9)	1125.7(3)	7.004	5.91
773	10.4053(9)	1126.6(3)	6.998	6.23
873	10.4159(8)	1130.0(3)	6.977	6.55
973	10.4214(9)	1131.8(3)	6.966	6.87
1073	10.4297(9)	1134.5(3)	6.950	7.19
1173	10.4245(8)	1132.8(3)	6.960	_
1273	10.4131(9)	1129.1(3)	6.983	_

tungsten oxide under investigation allows us to assign this pyrochlore to the class of medium-expansion compounds. In the range 1073–1123 K, a "break" is observed in the a=f(T) curve for CsTaWO₆ due to crystal I (cubic) \rightarrow crystal II (cubic) reversible transition. Physically, the anomaly can be related to the changing of cesium crystallographic position from 8b (3/8, 3/8, 3/8) to 32e (x, x, x) [22].

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2008.01.017.

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