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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 $T \to 0$ to 630 K. The structure of $CsTaWO_6$ is refined by the Rietveld method: space group $F\,d3m$, $Z = 8$, $a = 10.3793(2)$ Å, $V = 1118.14(4)$ Å^3. The high-temperature X-ray diffraction was used for the determination of temperature of phase transition and coefficient of thermal expansion.

Keywords: Cesium tantalum tungsten oxide; Adiabatic vacuum calorimetry; Heat capacity; Thermodynamic functions; X-ray diffraction

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 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 solid-state 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 $CsTaWO_6$ sample was recorded on a Shimadzu X-ray diffractometer XRD-6000 (Cu Kα radiation, geometry θ–2θ) in the 2θ 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 ±2%, then it decreased to ±0.5% as the temperature was rising to 40 K, and was equal to ±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 ±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 350 K in the adiabatic vacuum calorimeter with the error of ±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 $CsTaWO_6$ was refined assuming space group *F d3m*. The initial model included the atomic coordinates in the structure of $CsNbWO_6$ [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 X-ray diffraction patterns for $CsTaWO_6$, 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*
Z	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

$$R_{wp} = \left\{ \frac{\sum w_i [y_{i\mathrm{obs}} - y_{i\mathrm{calc}}]^2}{\sum w_i [y_{i\mathrm{obs}}]^2} \right\}^{1/2}; \quad R_p = \frac{\sum |y_{i\mathrm{obs}} - y_{i\mathrm{calc}}|}{\sum y_{i\mathrm{obs}}}.$$

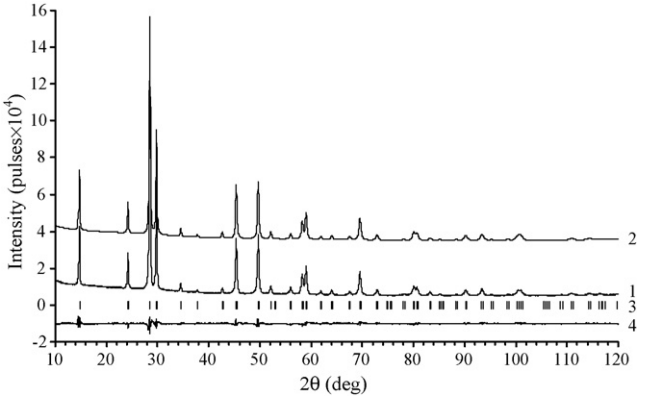

Fig. 1. Fragments of (1) observed, (2) simulated, and (4) difference X-ray diffraction patterns for $CsTaWO_6$ and (3) Bragg reflections. The simulated pattern is shifted relative to the observed pattern.

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 $CsTaWO_6$ structure. The $(Ta/W)O_6$ 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*	*y*	*z*	Occ	*B* (Å^2)
Cs	8b	0.375	0.375	0.375		1.52(4)
Ta	16c	0	0	0	0.5	0.75(2)
W	16c	0	0	0	0.5	0.75(2)
O	48f	0.3180(4)	0.125	0.125		0.75(2)