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Structural and thermochemical studies on Cr₂TeO₆ and Fe₂TeO₆

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Abstract

 Cr_2TeO_6 and Fe_2TeO_6 were prepared by the solid-state reaction route. The crystal structure was derived for both compounds from X-ray powder diffraction data. Cr_2TeO_6 and Fe_2TeO_6 are isostructural and have the trirutile structure. The Gibbs free energy of formation $(\Delta_f G^\circ)$ for Cr_2TeO_6 and Fe_2TeO_6 was obtained from vapor pressure data employing the Knudsen Effusion Mass Loss technique (KEML) and is given by the relation

 $\Delta_{\rm f} G^{\circ} {\rm Cr}_2 {\rm TeO}_6({\rm s}) = (-1651.6 + 0.5683T) \pm 15 \, {\rm kJ/mol} \, (1014 - 1100 \, {\rm K})$

 $\Delta_{\rm f} G^{\circ} {\rm Fe}_{2} {\rm TeO}_{6}({\rm s}) = (-1234.3 + 0.4729T) \pm 15 \, {\rm kJ/mol} \, (979 - 1052 \, {\rm K}).$

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1. Introduction

The structure and thermochemistry of binary and ternary oxides of uranium, plutonium and fission products formed during the irradiation of oxide fuels is important in evaluating their performance in a reactor [1]. Tellurium is one of the highly reactive fission products, which embrittles the stainless steel cladding components [2] containing Cr, Fe, Ni, Zr, Nb, etc. used in Fast Breeder Reactors (FBR). The binary phase diagram of M-Te systems (M=Fe, Cr, Ni, Mo, Nb, Zr, La, Ru and Ag) have been compiled and evaluated in the literature [3]. In the transition metal-tellurium-oxygen system, the formation of several compounds, through the solid-state reaction route, such as Cr₂Te₃O₉, Fe₂Te₃O₉, CoTeO₃, CoTe₆O₁₃, NiTeO₃, NiTe₂O₅ and Ni₂Te₃O₈, has been reported by Sokolov et al. [4]. Thermal and structural studies of the phase transformations of the tellurites of trivalent chromium and iron have been carried out by Gospodinov and Gjurova [5]. Recently, we reported the preparation, characterization and vaporization behavior of compounds in the Ni-Te-O system [6]. In continuation of our earlier investigations on the M-Te-O system, we report here a study of the crystal structure and measurement of the thermodynamic quantities of the tellurates of chromium and iron, namely Cr_2TeO_6 and Fe_2TeO_6 . The crystal structure was derived from X-ray powder diffraction data, whereas thermodynamic quantities such as enthalpy of vaporization and the standard Gibbs energy of formation were calculated from vapor pressure measurements over $Cr_2TeO_6(s)$ and $Fe_2TeO_6(s)$.

2. Experimental

2.1. Preparation and characterization of the compounds

 Cr_2TeO_6 and Fe_2TeO_6 were prepared by the solid-state reaction route by heating well-ground mixtures of Cr_2O_3 and Fe_2O_3 with TeO_2 in their respective molar ratios of 1:1 in the form of pressed pellets in an alumina boat in air at 975 K for 24 h. Samples were reground and refired twice to obtain single-phase compounds. The formation of the compounds was confirmed from their X-ray diffraction patterns recorded on a Diano X-ray diffractometer using graphite monochromatized Cu K α_1 radiation ($\lambda = 0.15406$ nm). The step-scanned intensity data was obtained in the 2θ range of 15 to 100° with a step of 0.02°, by counting for 5 s at each step. Refinement of the structure was carried

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Table 2

out by the Rietveld profile method using the computer program DBWS-9411 [7] for deriving the structure.

2.2. Thermal and vapor pressure measurements

The thermal stability of Cr_2TeO_6 and Fe_2TeO_6 was studied by recording the thermogravimetric (TG) patterns in air in a Mettler thermoanalyser at a heating rate of 10 K/min. The experiments were carried out in platinum cups in flowing dry air up to 1673 K.

Mass loss measurements were carried out in a Cahn Vacuum microbalance by the Knudsen Effusion Mass Loss (KEML) technique. A boron nitride cell with a knife edge orifice of approximately 1.0 mm diameter at the center of the lid was used as the Knudsen cell. The vapor pressures of $TeO_2(g)$ over $Cr_2TeO_6(s)$ and $Fe_2TeO_6(s)$ were measured in the temperature range 1014–1100 and 979–1052 K respectively. The experimental conditions were similar to those reported in our earlier studies on the Ni–Te–O system [6].

3. Results and discussion

3.1. X-ray studies

The X-ray diffraction data for these compounds were indexed on a tetragonal cell and the least squares refined values of the lattice parameters are given in Table 1. The X-ray powder diffraction data for Cr_2TeO_6 and Fe_2TeO_6 are in good agreement with the data reported in the literature [8]. The similarity in the X-ray powder patterns suggests that both the compounds are isostructural.

Oxides with the general formula A_2BO_6 are known to exist in the trirutile structure [9]. The crystal structure parameters for Cr_2TeO_6 and Fe_2TeO_6 were refined on the

Table 1

Rietveld refinement data for Cr₂TeO₆ and Fe₂TeO₆^a

Cr ₂ TeO ₆	Fe ₂ TeO ₆
327.6	335.3
P4/mnm	P4/mnm
0.45453(1)	0.46057(2)
0.45453(1)	0.46057(2)
0.90119(3)	0.90923(4)
2	2
-	-
15-100	15 - 100
0.02	0.02
0.15406	0.15406
4250	4250
Pseudo-Voigt	Pseudo-Voigt
8.79	10.45
11.15	8.53
8.64	7.81
1.29	1.33
	Cr ₂ 1eO ₆ 327.6 P4/mnm 0.45453(1) 0.45453(1) 0.90119(3) 2 - 15-100 0.02 0.15406 4250 Pseudo-Voigt 8.79 11.15 8.64 1.29

 ${}^{a}R_{p} = 100 \times \Sigma |y_{obs} - y_{cal}| / \Sigma |y_{obs}|; \quad R_{wp} = 100 \times \{ [\Sigma w (y_{obs} - y_{cal})^{2}] / [\Sigma w (y_{obs})^{2}] \}^{1/2}.$

Atomic parameters for Cr_2TeO_6 and Fe_2TeO_6 . Estimated standard deviations are given in parentheses

Atom	Site	x	у	Z	B (Å ²)
Cr. TeO.					
Cr	4e	0	0	0.3338(3)	0.67(6)
Те	2a	0	0	0	1.03(4)
01	4f	0.3058(13)	0.3058(13)	0	1.01(16)
O2	8 <i>j</i>	0.3082(8)	0.3082(8)	0.3359(8)	1.41(31)
Fe ₂ TeO ₆					
Fe	4e	0	0	0.3368(5)	0.74(7)
Те	2a	0	0	0	0.96(5)
01	4f	0.2937(24)	0.2937(24)	0	1.11(18)
O2	8 <i>j</i>	0.3097(15)	0.3097(15)	0.3346(16)	1.32(29)

basis of the trirutile structure by Rietveld profile analysis of the step-scanned X-ray intensity data. The variables include a scale factor, six background parameters, three half-width parameters defining the pseudo-Voigt profile peak shape, the unit cell dimensions, atomic positions, thermal parameters for chromium (or iron) and tellurium atoms. Details of refinement and agreement factors are given in Table 1. The structural parameters including fractional atomic coordinates and the isotropic thermal parameters of the atoms and selected inter-atomic distances for Cr_2TeO_6 and Fe_2TeO_6 are given in Tables 2 and 3, respectively. The observed, calculated and difference Xray powder diffraction pattern for Cr₂TeO₆ is shown in Fig. 1. The structures of Cr₂TeO₆ and Fe₂TeO₆ are similar and the structure of $Cr_2 TeO_6$ is shown in Fig. 2. In the structure, each Cr and Te atom is surrounded by six oxygen atoms in an octahedral coordination. The cation oxygen octahedra form edge-sharing chains which are occupied alternately by TeO₆ and CrO₆ octahedra in the ratio of 1:2.

3.2. Thermal studies

The TG curves in Figs. 3 and 4 show that both Cr_2TeO_6 and Fe_2TeO_6 are stable in air up to 1123 K. Cr_2TeO_6 decomposes rapidly in the range 1250–1350 K and the mass loss is complete at 1623 K. The decomposition of Fe_2TeO_6 takes place over a wider temperature range, 1200–1550 K, and is complete at 1673 K. The slow

Table	3								
Main	interatomic	distance	(Å)	for	M ₂ TeO ₆	(where	M = Cr	or	Fe)

	Cr ₂ TeO ₆	Fe ₂ TeO ₆
$Te-O_1 \times 2$	1.966 (6)	1.913 (11)
$Te-O_2 \times 4$	1.925 (6)	1.949 (11)
$M - O_1 \times 2$	1.950 (4)	2.002 (8)
$M-O_2 \times 2$	1.964 (6)	1.991 (8)
$M - O_2 \times 2$	1.981 (4)	2.017 (8)
M–M	2.996 (5)	2.968 (9)
M-Te	3.008 (3)	3.062 (5)



Two-Theta (degrees)

Fig. 1. Observed (\cdot) and calculated (----) X-ray diffraction Rietveld plot for Cr₂TeO₆. The difference curve is shown at the bottom of the plot.

decomposition of Fe_2TeO_6 in comparison to that of Cr_2TeO_6 suggests that the activation energy associated with the decomposition of Fe_2TeO_6 is more than that of



Fig. 2. Structure of Cr₂TeO₆ showing the coordination around Cr and Te.

 Cr_2TeO_6 . The final products of the decomposition of Cr_2TeO_6 and Fe_2TeO_6 , due to the combined loss of 1 mol of TeO_2 and 0.5 mol of O_2 , were identified by XRD as Cr_2O_3 and Fe_2O_3 , respectively. During decomposition, the observed mass losses of 53.9% for Cr_2TeO_6 and 52.8% for Fe_2TeO_6 are in good agreement with the expected losses of 53.6 and 52.4% as represented by Eqs. (1) and (2):

$$Cr_2TeO_6(s) \to Cr_2O_3(s) + TeO_2(g) + \frac{1}{2}O_2(g)$$
 (1)

$$\operatorname{Fe}_{2}\operatorname{TeO}_{6}(s) \to \operatorname{Fe}_{2}\operatorname{O}_{3}(s) + \operatorname{TeO}_{2}(g) + \frac{1}{2}\operatorname{O}_{2}(g)$$
(2)



Fig. 3. Thermogravimetric curve for the decomposition of $Cr_2TeO_6(s)$ under non-isothermal conditions in air at a heating rate of 10 K/min.



Fig. 4. Thermogravimetric curve for the decomposition of $Fe_2TeO_6(s)$ under non-isothermal conditions in air at a heating rate of 10 K/min.

3.3. Vapor pressure measurements

3.3.1. Cr_2TeO_6

The equilibrium pressures of $\text{TeO}_2(g)$ and $\frac{1}{2}\text{O}_2(g)$ measured in the temperature range 1014 to 1100 K over $\text{Cr}_2\text{TeO}_6(s)$ and $\text{Cr}_2\text{O}_3(s)$ were due to the combined loss of the gaseous products as represented in Eq. (1). The total mass loss due to $\text{TeO}_2(g)$ and $\frac{1}{2}\text{O}_2(g)$ was apportioned in terms of their individual masses using their mole fractions for the reaction given in Eq. (1). The mathematical derivation for the rate of mass loss (in g/s) is similar to that adopted for Ni_3TeO_6 [6] and is

$$dw/dt = dw_1/dt + dw_2/dt$$
(3)

$$dw_2/dt = (dw_1/dt)(32/159.6n)$$
(4)

where "dw/dt" is the experimentally measured combined rate of mass loss of TeO₂(g) and O₂(g), " dw_1/dt " and " dw_2/dt " are the individual rates of mass loss of TeO₂(g) and O₂(g), respectively, and "*n*" is the ratio of number of moles of TeO₂(g) to O₂(g), which is equal to 2 in the present study. Substituting the value of " dw_2/dt " in Eq. (3) and rearranging, we obtain

$$dw_1/dt = (dw/dt)(159.6/175.6) = (dw/dt)0.9089$$
(5)

By substituting the individual mass loss of $TeO_2(g)$ and $O_2(g)$ in the rate mass equation:

$$p (Pa) = dw/dt [1/kA] (2.28 \times 10^{-3}) \sqrt{T/M}$$
(6)

the individual partial pressures contributed by $\text{TeO}_2(g)$ and $O_2(g)$ were determined and are given in Table 4. The corresponding least squares fit between log *p* and 1/T for TeO_2 is shown in Fig. 5 and can be represented by the relation

Table 4	
Gibbs energy of formation of $Cr_2TeO_6(s)$ at different ten	nperatures

Temp. (K)	$p(\text{TeO}_2)$ (Pa)	$p^{\circ}(\text{TeO}_2)$ (Pa)	$p(O_2)$ (Pa)	$\Delta_{\rm f}G^{\circ}{ m Cr}_{2}{ m TeO}_{6}({ m s})$ (kJ/mol)
1014	0.447	18.226	0.100	-1076.9
1021	0.627	21.695	0.140	-1071.8
1028	0.771	25.764	0.173	-1068.3
1034	1.003	29.799	0.224	-1064.2
1040	1.294	34.408	0.290	-1060.2
1048	1.719	41.573	0.385	-1055.4
1053	2.093	46.722	0.460	-1052.2
1059	2.700	53.672	0.605	-1048.0
1066	3.152	62.973	0.706	-1045.0
1072	3.951	72.098	0.884	-1041.2
1079	4.881	84.268	1.093	-1037.3
1092	5.739	111.980	1.284	-1033.2
1100	7.657	132.950	1.714	-1028.1

log
$$p$$
 (kPa) = (-15920.14/T
+ 12.408)±0.04 (1014-1100 K) (7)

The standard Gibbs free energy of the reaction shown in Eq. (1) can be represented as

$$\Delta_{\rm r}G^{\circ} = \Delta_{\rm f}G^{\circ}{\rm Cr}_2{\rm O}_3({\rm s}) + \Delta_{\rm f}G^{\circ}{\rm TeO}_2({\rm g}) + \frac{1}{2}\Delta_{\rm f}G^{\circ}{\rm O}_2({\rm g}) - \Delta_{\rm f}G^{\circ}{\rm Cr}_2{\rm TeO}_6({\rm s})$$
(8)

Substituting $\Delta_{\rm r}G^{\circ} = -RT \ln K$ and rearranging Eq. (8), we obtain

$$\Delta_{f}G^{\circ}Cr_{2}TeO_{6}(s) = \Delta_{f}G^{\circ}Cr_{2}O_{3}(s) + \Delta_{f}G^{\circ}TeO_{2}(l) + \frac{1}{2}RT \ln pO_{2}(g) + RT \ln(pTeO_{2}/p^{\circ}TeO_{2})$$
(9)

where $p^{\circ}\text{TeO}_2$ is the partial pressure of $\text{TeO}_2(g)$ over $\text{TeO}_2(1)$. The values of the Gibbs free energy of formation for $\text{Cr}_2\text{O}_3(s)$ and $\text{TeO}_2(1)$ are taken from the literature [10,11]. Using the above values, the Gibbs free energy of formation of Cr_2TeO_6 was calculated and is given in Table 4, and can be represented by the relation



Fig. 5. Temperature dependence of the vapor pressure of $TeO_2(g)$ over $Cr_2TeO_6(s)$ and $Cr_2O_3(s)$.

Table 5 Gibbs energy of formation of $\text{Fe}_2\text{TeO}_6(s)$ at different temperatures

Temp.	$p(\text{TeO}_2)$	$p^{\circ}(\text{TeO}_2)$	$p(O_2)$	$\Delta_{\rm f} G^{\circ} {\rm Fe}_{2} {\rm TeO}_{6}({\rm s})$
(K)	(Pa)	(Pa)	(Pa)	(kJ/mol)
979	1.218	7.346	0.273	-769.8
983	1.427	8.177	0.319	-767.4
992	1.490	10.372	0.333	-765.9
998	1.766	12.126	0.395	-763.1
1002	1.819	13.443	0.407	-762.2
1006	2.187	14.890	0.489	-760.4
1011	2.450	16.902	0.549	-757.4
1020	3.197	21.165	0.716	-752.9
1028	3.948	25.764	0.884	-749.2
1032	6.115	28.394	1.370	-743.1
1043	7.204	36.949	1.612	-739.5
1052	7.646	45.648	1.712	-737.6

$$\Delta_{f}G^{\circ}Cr_{2}TeO_{6}(s) = (-1651.6 + 0.56833T)$$

$$\pm 15 \text{ kJ/mol} (1014 - 1100 \text{ K})$$
(10)

3.3.2. Fe₂TeO₆

The individual mass loss of $\text{TeO}_2(g)$ and $\frac{1}{2}\text{O}_2(g)$ over Fe_2TeO_6 and $\text{Fe}_2\text{O}_3(s)$ was obtained by the method adopted for $\text{Cr}_2\text{TeO}_6(s)$. The individual partial pressures of $\text{TeO}_2(g)$ and $\text{O}_2(g)$ are given in Table 5, and the corresponding least squares fit between "log *p*" and 1/T for TeO_2 is shown in Fig. 6, and can be represented by the relation

$$\log p \text{ (kPa)} = (-12283.9/T + 9.582) \pm 0.06 (979 - 1052 \text{ K})$$
(11)

The standard Gibbs free energy of the reaction shown in Eq. (2) is given by the relation

$$\Delta_{\rm r}G^{\circ} = \Delta_{\rm f}G^{\circ}{\rm Fe}_2{\rm O}_3({\rm s}) + \Delta_{\rm f}G^{\circ}{\rm TeO}_2({\rm g}) + \frac{1}{2}\Delta_{\rm f}G^{\circ}{\rm O}_2({\rm g}) - \Delta_{\rm f}G^{\circ}{\rm Fe}_2{\rm TeO}_6({\rm s})$$
(12)



Fig. 6. Temperature dependence of the vapor pressure for $TeO_2(g)$ over $Fe_2TeO_6(s)$ and $Fe_2O_3(s)$.

Substituting $\Delta_r G^\circ = -RT \ln K$ and rearranging the above equation:

$$\Delta_{f}G^{\circ}Fe_{2}TeO_{6}(s) = \Delta_{f}G^{\circ}Fe_{2}O_{3}(s) + \Delta_{f}G^{\circ}TeO_{2}(l) + \frac{1}{2}RT \ln pO_{2}(g) + RT \ln(pTeO_{2}/p^{\circ}TeO_{2})$$
(13)

where $p^{\circ}\text{TeO}_2$ is the partial pressures of $\text{TeO}_2(g)$ over $\text{TeO}_2(1)$. The values of the Gibbs free energy of formation for $\text{Fe}_2\text{O}_3(s)$ and $\text{TeO}_2(1)$ are taken from the literature [10,11]. The values of the Gibbs free energy of formation for Fe_2TeO_6 are given in Table 5 and can be represented by the relation

$$\Delta_{\rm f} G^{\circ} {\rm Fe}_{2} {\rm TeO}_{6}({\rm s}) = (-1234.3 + 0.47286T)$$

±15 kJ/mol (979–1052 K). (14)

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