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X-ray and thermal investigations of $LaFeTeO_6$ and $LaCrTeO_6$ compounds

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Abstract

$LaFeTeO_6$ and $LaCrTeO_6$ were prepared by the solid-state reaction of La_2O_3, M_2O_3 (M = Fe or Cr) and TeO_2 in 1:1:2 molar ratio. The compounds were characterised by X-ray and thermogravimetric techniques. Thermal and X-ray studies indicated that $LaFeTeO_6$ and $LaCrTeO_6$ vapourize incongruently according to the reactions:

$$LaFeTeO_6(s) \rightarrow LaFeO_3(s) + TeO_2(g) + (1/2)O_2(g)$$

$$LaCrTeO_6(s) \rightarrow LaCrO_3(s) + TeO_2(g) + (1/2)O_2(g)$$

X-ray diffraction data of both the compounds have been indexed on the hexagonal system. Vapour pressures of $TeO_2(g)$ over $LaFeO_3(s)$ and $LaCrO_3(s)$ were independently measured by employing the Knudsen effusion mass loss (KEML) technique. From the partial pressures of $TeO_2(g)$ measured, the standard Gibbs free energy of formation of ($\Delta_f G^\circ$) $LaFeTeO_6(s)$ and $LaCrTeO_6(s)$ were obtained and could be represented by the following relations:

$$\Delta_f G^\circ(LaFeTeO_6(s)) \pm 15\,\mathrm{kJ/mol} = -1902.0 + 0.5953T \quad (1104\text{–}1205\,\mathrm{K}),$$

$$\Delta_f G^\circ(LaCrTeO_6(s)) \pm 12\,\mathrm{kJ/mol} = -612.0 + 0.3488T \quad (1106\text{–}1210\,\mathrm{K})$$

Keywords: Knudsen effusion mass loss technique; $LaFeTeO_6$; $LaCrTeO_6$

1. Introduction

Tellurium is one of the highly corrosive fission products that can interact with clad components, fissile elements and other fission products of the oxide fuels within the reactor forming binary and ternary oxides [1]. A number of uranates of strontium and tellurium are reported in the literature [2,3]. Also, the preparation of tellurates with the general formula $M_3UO_2(TeO_3)_4$ and $M_2U(TeO_3)_5$ where M = Ba or Ca, was reported [4]. However, there is no such data available in the literature on quaternary systems with lanthanum as one of the components though lanthanum is one of the prominent daughter products during fission. In continuation of our earlier studies on the ternary systems of tellurium bearing compounds [5–7], we report here, the X-ray, thermal and Gibbs free energy of formation of the two new phases $LaFeTeO_6$ and $LaCrTeO_6$.

2. Experimental

2.1. Preparation and characterisation of the compounds

$LaFeTeO_6$ and $LaCrTeO_6$ were prepared by heating a mixture of La_2O_3, M_2O_3 (M = Fe or Cr) and TeO_2 in 1:1:2 molar ratios in air at 1200 K. The

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products were removed intermittently, ground and reheated to obtain pure phases of the compounds. The formation of the compounds were confirmed by recording their X-ray diffraction patterns on a STOE X-ray diffractometer using graphite monochromatised Cu Kα_1 radiation ($\lambda = 0.15406$ nm).

2.2. TG measurements

The thermal stability of $LaFeTeO_6$(s) and $LaCrTeO_6$(s) were studied by recording their TG patterns with a Cahn microbalance thermal analyser. The experiments were carried out in air in boron nitride cups at the heating rate of 10 K/min up to 1475 K. Both the compounds were found to be stable up to 1100 K beyond which the vapourization of the compounds is initiated. The final products at the end of the reaction were identified by X-ray powder diffraction method as $LaFeO_3$ in the case of $LaFeTeO_6$ and $LaCrO_3$ with $LaCrTeO_6$. Their thermal decomposition in air could be represented as

$$LaFeTeO_6(s) \rightarrow LaFeO_3(s) + TeO_2(g) + (1/2)O_2(g) \quad (1)$$

$$LaCrTeO_6(s) \rightarrow LaCrO_3(s) + TeO_2(g) + (1/2)O_2(g) \quad (2)$$

2.3. Vapour pressure measurements

The mass loss measurements due to vapourization were carried out in a Cahn vacuum microbalance by the Knudsen effusion mass loss (KEML) technique. Boron nitride cell with an orifice diameter of ≈1.0 mm at the center of the lid was used as the Knudsen cell. Detailed experimental set-up and the Clausing factor calibration for the Knudsen cell have been described in our earlier studies [8].

3. Results and discussion

3.1. X-ray and thermal studies

The products formed by reacting La_2O_3, M_2O_3 (M = Fe or Cr) and TeO_2 in 1:1:2 molar ratio in air at 1200 K were characterised by XRD. X-ray diffraction data of $LaCrTeO_6$ in the present study matched well with the data reported by Kaspar [9]. The X-ray powder diffraction data of $LaFeTeO_6$ could also be indexed on the hexagonal system as they are iso-structural. Their unit cell parameters were refined by the least squares method using the computer program LATPAR [10]. The indexed diffraction data of both the compounds are given in Tables 1 and 2.

3.2. Vapour pressure measurements

3.2.1. $LaFeTeO_6$

The equilibrium vapour pressures of TeO_2(g) and (1/2)O_2(g) were measured in the temperature range 1104 to 1205 K over a mixture of $LaFeTeO_6$(s) by employing the Knudsen effusion mass loss (KEML) technique. The detailed experimental set-up of KEML is similar to our earlier reported results in [6]. The total mass loss due to TeO_2(g) and (1/2)O_2(g) was apportioned in terms of their molar masses using their mole fraction for reaction (1) and could be given as

$$\mathrm{d}w/\mathrm{d}t = \mathrm{d}w_1/\mathrm{d}t + \mathrm{d}w_2/\mathrm{d}t \quad (3)$$

where $\mathrm{d}w/\mathrm{d}t$ is the experimentally measured combined rate of mass loss of TeO_2(g) and (1/2)O_2(g), $\mathrm{d}w_1/\mathrm{d}t$ and $\mathrm{d}w_2/\mathrm{d}t$ are the individual rate of mass loss of TeO_2(g) and (1/2)O_2(g), respectively. Similar apportionation procedure has been followed in our earlier studies on Ni_3TeO_6 compound in Ni–Te–O system and Cr_2TeO_6 and Fe_2TeO_6 in Cr/Fe–Te–O systems [6,11]. The mathematical derivation for the rate of mass loss is given below:

$$\mathrm{d}w/\mathrm{d}t \ = \mathrm{d}w_1/\mathrm{d}t + \mathrm{d}w_2/\mathrm{d}t \quad (3)$$

Table 1
X-ray powder diffraction data on $LaCrTeO_6$ indexed on hexagonal system with cell parameters $a = 5.1578(7)$ Å, $c = 10.3722(15)$ Å

h k l	*d* (observed) (Å)	*d* (calculated) (Å)	I/I_0
0 0 2	5.1798	5.1861	6
1 0 0	4.4593	4.4668	6
1 0 2	3.3805	3.3845	100
1 1 0	2.5767	2.5789	30
1 1 2	2.3072	2.3092	4
1 0 4	2.2399	2.2426	4
2 0 2	2.0493	2.0513	19
1 1 4	1.8278	1.8285	32
1 0 6	1.6118	1.6112	9
2 1 2	1.6050	1.6054	17
3 0 0	1.4884	1.4889	8
3 0 3	1.3669	1.3675	5
2 0 6	1.3669	1.3670	5
0 0 8	1.2966	1.2965	2
2 2 0	1.2901	1.2895	6
2 1 6	1.2076	1.2078	6
3 1 2	1.2049	1.2050	8
1 1 8	1.1584	1.1584	4
2 2 4	1.1548	1.1546	6
4 0 2	1.0915	1.0917	2
1 0 10	1.0105	1.0103	2
3 1 6	1.0071	1.0070	3
3 2 2	1.0051	1.0053	3
3 0 8	0.9778	0.9778	2
4 1 0	0.9750	0.9747	3

Table 2
X-ray powder diffraction data on $LaFeTeO_6$ indexed on hexagonal system with cell parameters, $a = 5.2017(4)$ Å, $c = 10.3393(12)$ Å

h k l	*d* (observed) (Å)	*d* (calculated) (Å)	I/I_0
0 0 2	5.1706	5.1697	5
1 0 0	4.5019	4.5048	3
1 0 1	4.1286	4.1298	4
1 0 2	3.3950	3.3963	100
1 1 0	2.5993	2.6008	34
1 1 2	2.3225	2.3234	6
1 0 4	2.2426	2.2420	3
2 0 2	2.0641	2.0649	23
1 1 4	1.8329	1.8334	39
2 1 2	1.6170	1.6172	22
3 0 0	1.5016	1.5016	12
2 0 6	1.3682	1.3686	5
3 0 4	1.2985	1.2984	8
3 1 2	1.2146	1.2144	8
2 1 6	1.2113	1.2112	10
2 2 4	1.1618	1.1617	6
4 0 2	1.1004	1.1004	3
3 2 2	1.0134	1.0134	4
3 1 6	1.0114	1.0115	5
4 1 0	0.9831	0.9830	3
3 0 8	0.9797	0.9796	4

Table 3
Gibbs free energy of formation of $LaFeTeO_6$ at different temperatures

Temperature (K)	$p(TeO_2)$ (Pa)	$p^\circ(TeO_2)$ (Pa)	$p(O_2)$ (Pa)	$\Delta_f G^\circ(LaFeTeO_6)$ (kJ/mol)
1104	0.4172	144.7319	0.2043	−1244.78
1132	1.1080	257.8357	0.5426	−1228.12
1136	1.2676	279.3570	0.6224	−1255.74
1145	1.6575	333.8927	0.8641	−1220.38
1150	2.0004	368.2218	0.9849	−1217.41
1152	2.1888	382.8312	1.0738	−1203.71
1165	3.2923	491.3923	1.6165	−1208.48
1173	4.4824	571.4187	2.2025	−1203.71
1175	4.6056	593.1937	2.2640	−1202.52
1180	5.2440	650.9700	2.5764	−1199.55
1205	11.4456	1024.1379	5.6311	−1184.66

$$dw_2/dt = dw_1/dt \times 1/2 \times \sqrt{32/159.6} \tag{4}$$

$$dw_1/dt = (dw/dt)(0.819) \tag{5}$$

By substituting the value of dw_1/dt in Eq. (4), we can calculate dw_2/dt. Thus by inserting the individual mass loss of dw_1/dt and dw_2/dt in the rate mass loss equation (3)

$$p\,(\mathrm{Pa}) = [(dw/dt)(1/kA)\sqrt{T/M}] \tag{6}$$

where p is the partial pressures of the evolved gas, k the Clausing factor, A the area of the orifice diameter, T the temperature and M is the molecular weight of the evolved gaseous species, the individual partial pressures contributed by $TeO_2(g)$ and $O_2(g)$ were determined and are given in Table 3. The corresponding least squares fit of $\log p(TeO_2(g))$ versus $1/T$ is shown in Fig. 1 and could be represented by the relation:

$$\log p\,(\mathrm{kPa}) \pm 0.01 = -43\,742/T + 31.1694 \quad (1104\text{–}1205\,\mathrm{K}) \tag{7}$$

The standard Gibbs free energy of formation of $LaFeTeO_6(s)$ is represented by the relation:

$$\begin{aligned}&\Delta_f G^\circ(LaFeTeO_6(s))\\&\quad = \Delta_f G^\circ(LaFeO_3(s)) + \Delta_f G^\circ(TeO_2(l)) + 0.5RT \ln p(O_2(g))\\&\qquad + RT \ln(p(TeO_2)/p^\circ(TeO_2))\end{aligned} \tag{8}$$

Where $p^\circ(TeO_2)$ is the partial pressure of $TeO_2(g)$ over $TeO_2(l)$ and the vapour pressure data are taken from reported values [12]. By using the Gibbs free energy formation of $TeO_2(l)$ and that of $LaFeO_3$ from the literature data [1,13], the standard Gibbs free energy formation of $LaFeTeO_6(s)$ could be obtained and is represented by the relation:

$$\begin{aligned}&\Delta_f G^\circ(LaFeTeO_6(s)) \pm 15\,\mathrm{kJ/mol}\\&\quad = -1902.0 + 0.5953T \quad (1104\text{–}1205\,\mathrm{K})\end{aligned} \tag{9}$$

3.2.2. $LaCrTeO_6$

The equilibrium vapour pressures of $TeO_2(g)$ over $LaCrO_3(s)$ were calculated at various temperatures (1106–1210 K) for the reaction shown in Eq. (2) and the values are given in Table 4. The corresponding least squares fit of $\log p(TeO_2(g))$ against $1/T$ for $LaCrTeO_6$ is shown in Fig. 2, which could be represented by the relation:

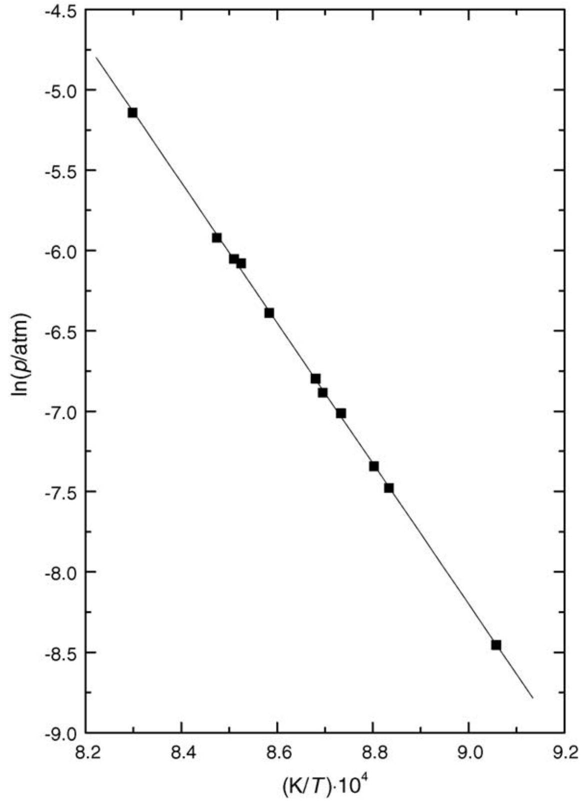

Fig. 1. Temperature dependence of the partial pressures of $TeO_2(g)$ over $LaFeTeO_6(s)$ and $LaFeO_3(s)$.

$$\log p\,(\mathrm{kPa}) \pm 0.01 = -42\,994/T + 30.0024 \quad (1106\text{–}1210\,\mathrm{K}) \tag{10}$$

By using the vapour pressure data of $TeO_2(g)$, the standard Gibbs free energy formation data of $LaCrTeO_6(s)$ could be obtained

Table 4
Gibbs free energy of formation of $LaCrTeO_6$ at different temperatures

Temperature (K)	$p(TeO_2)$ (Pa)	$p^\circ(TeO_2)$ (Pa)	$p(O_2)$ (Pa)	$\Delta_f G^\circ(LaCrTeO_6)$ (kJ/mol)
1106	0.3411	150.9726	0.2043	−226.23
1123	0.5943	214.8322	0.2958	−220.30
1127	0.6971	233.0640	0.3471	−218.90
1136	0.8776	279.3570	0.4364	−215.76
1138	0.9578	290.7207	0.4762	−215.06
1140	0.9586	302.5044	0.6244	−214.37
1148	1.2945	354.1220	0.6436	−211.58
1150	1.3327	368.2218	0.6437	−210.88
1158	1.7168	429.8830	0.8545	−208.09
1172	2.8929	560.8060	1.4405	−203.21
1185	4.1820	713.8136	2.0823	−198.67
1199	6.6021	920.1858	3.2876	−193.79
1209	9.1828	1099.2354	4.5676	−190.30
1210	9.3702	1118.7733	4.6661	−189.95

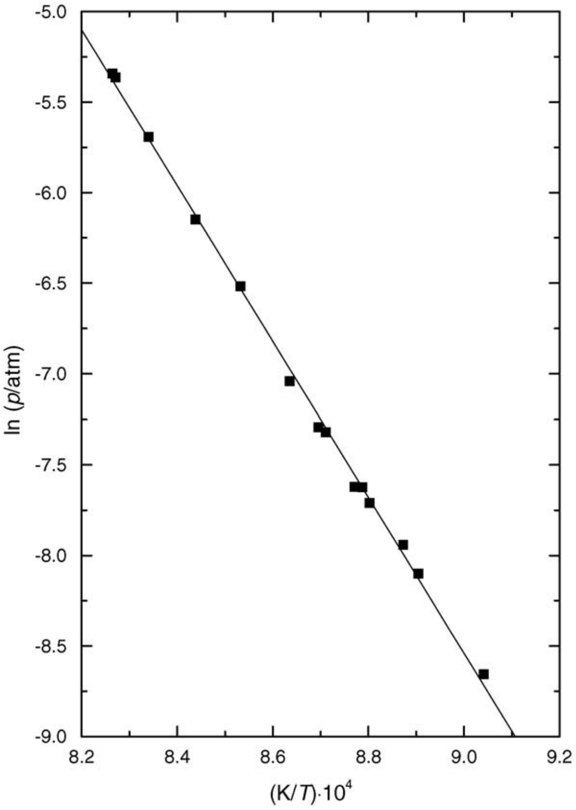

Fig. 2. Temperature dependence of partial pressures of $TeO_2(g)$ over $LaCrTeO_6(s)$ and $LaCrO_3(s)$.

from the relation:

$$\Delta_f G^\circ(\mathrm{LaCrTeO_6(s)}) = \Delta_f G^\circ(\mathrm{LaCrO_3(s)}) + \Delta_f G^\circ(\mathrm{TeO_2(l)}) + 0.5RT\ln p(\mathrm{O_2(g)}) + RT\ln(p(\mathrm{TeO_2})/p^\circ(\mathrm{TeO_2})) \quad (11)$$

Using the values of $p^\circ(TeO_2)$ from our earlier studies [12], the Gibbs free energy formation data of $TeO_2(l)$ from the literature [13] the Gibbs free energy formation of $LaCrTeO_6(s)$ was calculated and the data are given in Table 4, which is represented by the relation:

$$\Delta_f G^\circ(\mathrm{LaCrTeO_6(s)}) \pm 12\,\mathrm{kJ/mol} = -612.0 + 0.3488T \quad (1106\text{–}1210\,K) \quad (12)$$

4. Conclusion

The data on the Gibbs free energy of formation of the compounds $LaFeTeO_6$ and $LaCrTeO_6$ are being reported for the first time in the La–M–Te–O system. Both the compounds have been indexed on the hexagonal system and their lattice cell parameters were refined.

From the TG studies, it was observed that both the compounds vapourize incongruently with the loss of TeO_2 and the final products were identified as $LaFeO_3$ in the case of $LaFeTeO_6$ and $LaCrO_3$ in the case of $LaCrTeO_6$.

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