Synthesis and Study of Thermodynamic Functions of Sodium Tellurite Compounds

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Abstract

Na_2TeO_3 (s), $Na_2Te_2O_5$ (s) and $Na_2Te_4O_9$ (s) were synthesized by solid state reaction route and characterized using X-ray powder diffraction method. Standard molar heat capacity values of these oxides were measured in the temperature range 325-675 K using differential scanning calorimeter (DSC). The experimental data are statistically processed using the least squares method to obtain the equation for the corresponding compounds. From these data, standard thermodynamic functions such as enthalpy increment (H^o_T - $H^o_{298.15}$), entropy (S^o_T) and Gibbs energy functions (fef) were computed.

Keywords: Heat capacity, sodium tellurites, DSC, Thermodynamic function.

Introduction

Sodium (Na) and its alloys have been used as coolant components in the liquid metal fast breeder reactor (LMFBR). A 500 MWe sodium cooled Prototype Fast Breeder Reactor (PFBR) is being set up in India, where $(U,Pu)O_2$ is proposed as the fuel [1]. During the fission of MOX fuel, tellurium (Te) gets generated as one of the fission products with moderate fission yield. The presence of highly corrosive Te in the fuel-clad gap has been reported by many investigators [2–8]. In nuclear reactor accidents, understanding the behavior of fission products are important in order to determine their potentials for radioactive release. The release of fission products from the fuel matrix can be predicted from the thermodynamic data of relevant compounds containing the fission products. Hence, the studies of tellurium bearing compounds which could be formed by all possible interactions between fuels, fission products, clad and coolant, during reactor operation is important in understanding and evaluating the performance of MOX fuel of the PFBR [9-10]. In case of clad breach, there is a chance of formation of compounds in Na-Te-O system. Hence the thermodynamic stability of sodium tellurites needs to be investigated in detail. Na_2TeO_3 (s), $Na_2Te_2O_5$ (s) and $Na_2Te_4O_9$ (s) are important compounds in the ternary system of Na-Te(IV)-O. Chattopadhyay et al. determined the thermal properties of various compounds which may be formed as the result of interaction of cladding material components with tellurium and oxygen [11].

In the present work, the Na_2TeO_3 (s), $Na_2Te_2O_5$ (s) and $Na_2Te_4O_9$ (s) are synthesized using solid state reaction route and characterized using X-ray diffraction techniques. The standard molar heat capacity is determined using differential scanning calorimeter (DSC) in temperature range 325 to 675 K. From the experimental molar heat capacities, standard thermodynamic functions such as enthalpy increment, entropy and Gibbs free energy functions (fef) were evaluated. Heat capacity of a material is an important thermodynamic property describing the relation between heat and temperature, and is therefore of crucial importance for materials engineering. In addition, thermal conductivity of any material, derived from

known heat capacity, density and diffusivity data, is also an important parameter for rector designers and used in predicting fuel performance inside the reactor.

Materials and Methods:

Sample Preparation and Characterization:

Na_2TeO_3 (s), $Na_2Te_2O_5$ (s) and $Na_2Te_4O_9$ (s) were synthesized by solid-state reaction route. The Na_2CO_3 (s) and TeO_2 (s) of 99.9 % purity obtained from M/s. Alfa Aesar, USA were used as a starting reactant for preparation of these compounds. The required stoichiometric amounts of reactants were mixed thoroughly in an agate mortar. The mixtures were compacted into pellets of 5 mm diameter and 2 mm thickness under a pressure of 100 MPa with hydraulic press. The pellet of these mixed oxides were kept in separate alumina boats and heated at 873 K for 12 h in flowing argon atmosphere. For homogenization and pure phase formation, the reactant mixture was cooled intermittently and re-ground. The resulting powder was re-pelletized and heated at 1023 K for 24 h under flowing argon atmosphere and annealed to 673 K for 30 minutes. The samples were furnace cooled to room temperature and characterized by X-ray diffractometry (XRD) using Cu Kα radiation ($\lambda = 1.5406$ A^o, model: miniflex-600, M/s. Rigaku, Japan). The XRD patterns were taken in the 2θ scans range: $5^o \leq 2\theta \leq 80^o$. XRD patterns of Na_2TeO_3 (s), $Na_2Te_2O_5$ (s) and $Na_2Te_4O_9$ (s) are shown in Fig. 1. The formation of compounds were confirmed by comparing the recorded X-ray diffraction (XRD) patterns of samples with the JCPDS (joint committee on powder diffraction standards) pattern and were found to match exclusively with that reported in literature [12] having file nos. 01-0152, 51-1829 and 28-1140 respectively.
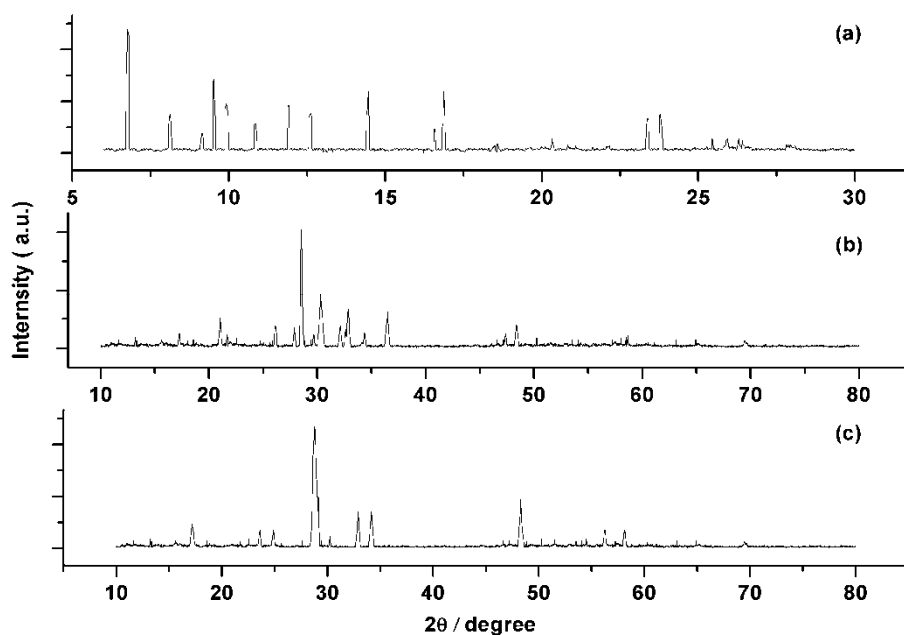

Fig. 1. X-ray diffraction patterns of: (a) Na_2TeO_3 (b) $Na_2Te_2O_5$ and (c) $Na_2Te_4O_9$.

Heat Capacity Measurement:

The heat flux differential scanning calorimeter (Model:Labsys Evo) supplied by M/s. Setaram Instrumentation, France, has been used for heat capacity measurement of Na_2TeO_3 (s), $Na_2Te_2O_5$ (s) and $Na_2Te_4O_9$ (s). Differential scanning calorimeter (DSC) is widely used to measure heat capacity of variety of compounds such as ceramics, organic materials, polymers, ionic liquids etc.[13-18]. The details of experimental assembly, procedure followed for heat capacity measurement, the temperature calibration, heat flow calibration and instrument standardization are reported in literature [19-21]. Two empty, flat bottomed cylindrical platinum crucibles with covering lids of identical masses were selected for the sample and reference cells. NIST synthetic sapphire (SRM-720) in powder form was used as reference material for heat capacity measurement. Heating rate was maintained at 5 K min^{-1} using high purity argon as carrier gas with flow rate of 30 ml/min. Classical three-step method in the continuous heating mode was used to determine the heat capacity of the compound. In the first run both the sample and reference cells were loaded with empty platinum crucibles. The heat flow versus temperature was measured. In the second run a known weight of NIST synthetic sapphire (SRM 720) was loaded in the sample cell, keeping the crucible in the reference side empty and once again the heat flow versus temperature was measured in the same temperature range and at the same heating rate. In the third run, a known weight of the sample was loaded in the sample cell, reference cell being empty and once again the heat flow as a function of temperature was measured. All three sets of experiments were performed under identical experimental conditions viz. heating rate, carrier gas flow rate and temperature range. About 300 mg of sample size was used for the measurement of standard molar heat capacity in the temperature range of 325 to 675 K. Specific heat capacity of the sample under investigation can be calculated by a simple comparison of the heat flow rates in three runs as illustrated in the literature [21]. The heat capacity of Al_2O_3, Fe_2O_3 (mass fraction, 0.998) were measured in the temperature range of 300 to 700 K and compared with the literature values in order to check the accuracy of measurement and was found to be ± 2%. The XRD pattern of compounds before and after the experiment remained the same indicating the stability of the compounds under study. The standard molar heat capacity of Na_2TeO_3 (s), $Na_2Te_2O_5$ (s) and $Na_2Te_4O_9$ (s) were measured in the temperature range from 325 to 675 K.

Results and Discussion

The molar heat capacity values for Na_2TeO_3 (s), $Na_2Te_2O_5$ (s) and $Na_2Te_4O_9$ (s) measured experimentally in the temperatures ranges 325-675 K are given in Tables 1, 2 and 3 respectively. The experimental data are statistically processed using the least squares method to determine the parameters in the equations: $C^o_{p,m}$= a+b(T/K)-c(T/K)$^{-2}$ for the corresponding compounds as reported in literature [22] and given by the following equation,

$C^o_{p,m}$(Na_2TeO_3, s, T) /J K^{-1} mol^{-1} = 152.00 + 0.03 (T / K) – 3.12 x 10^6 (T / K)$^{-2}$ (1)

$C^o_{p,m}$($Na_2Te_2O_5$, s, T) /J K^{-1} mol^{-1} = 242.50 + 0.01 (T / K) – 5.12 x 10^6 (T / K)$^{-2}$ (2)

$C^o_{p,m}$($Na_2Te_4O_9$, s, T) /J K^{-1} mol^{-1} = 411.23 + 0.002 (T / K) – 9.84 x 10^6 (T / K)$^{-2}$ (3)

It can be seen that molar heat capacities follows the trend $Na_2Te_4O_9 > Na_2Te_2O_5 > Na_2TeO_3$. This trend can be explained on the basis of different thermal expansion behavior of these oxides which will give rise to difference in dilational contribution to the total heat capacity. Based on measured molar heat capacity, other thermodynamic functions such as H^o_T- $H^o_{298.15}$, S^o_T and fef for Na_2TeO_3 (s), $Na_2Te_2O_5$ (s) and $Na_2Te_4O_9$ (s) were derived using method described in an earlier publication [23-24]. The H^o_T- $H^o_{298.15}$ and S^o_T functions were calculated by numerical integration of the $C^o_{p,m}$ (T) and $C^o_{p,m}$ $(T)/T$ functions. The $S^o_{298.15}$ value for Na_2TeO_3 (s) require for above calculation were taken from literature [6]. The $S^o_{298.15}$ data

for $Na_2Te_2O_5$ (s) and $Na_2Te_4O_9$ (s) are not available, hence they were estimated in the present study by additive oxide method [24] which results 223.14 J K^{-1} mol^{-1} for $Na_2Te_2O_5$ (s) and 371.24 J K^{-1} mol^{-1} for $Na_2Te_4O_9$ (s). The $S^o_{298.15}$ value for Na_2O (s) and TeO_2(s) were taken from reported data [24]. The thermodynamic functions such as $C^o_{p,m}$, H^o_T- $H^o_{298.15}$, S^o_T and fef are tabulated in Tables 1-3 to generate the thermodynamic data for the compounds Na_2TeO_3 (s), $Na_2Te_2O_5$ (s) and $Na_2Te_4O_9$ (s), respectively.

Table 1 Standard thermodynamic functions of Na_2TeO_3 (s).

T K	$C^o_{p,m}$ J K^{-1} mol^{-1}		H^o_T - $H^o_{298.15}$ J mol^{-1}	S^o_T J K^{-1} mol^{-1}	fef J K^{-1} mol^{-1}
	Measured	Fit			
325	132.84	132.21	3467.65	174.24	163.57
350	138.28	137.03	6835.06	184.22	164.69
375	140.25	141.06	10312.65	193.82	166.32
400	144.28	144.50	13883.27	203.03	168.32
425	146.25	147.48	17533.82	211.88	170.63
450	150.72	150.09	21254.10	220.39	173.16
475	153.25	152.42	25036.07	228.57	175.86
500	154.89	154.52	28873.27	236.44	178.69
525	155.40	156.43	32760.50	244.03	181.63
550	159.10	158.19	36693.50	251.34	184.63
575	160.01	159.81	40668.73	258.41	187.68
600	161.28	161.33	44683.27	265.25	190.77
625	162.76	162.76	48734.65	271.86	193.89
650	163.02	164.12	52820.77	278.27	197.01
675	165.28	165.40	56939.87	284.49	200.13

Table 2 Standard thermodynamic functions of $Na_2Te_2O_5$ (s).

T K	$C^o_{p,m}$ J K^{-1} mol^{-1}		H^o_T - $H^o_{298.15}$ J mol^{-1}	S^o_T J K^{-1} mol^{-1}	fef J K^{-1} mol^{-1}
	Measured	Fit			
325	196.98	197.27	5176.08	239.77	223.85
350	203.89	204.20	10197.68	254.66	225.52
375	209.52	209.84	15375.57	268.94	227.94
400	213.87	214.50	20681.61	282.64	230.94
425	218.42	218.40	26094.29	295.76	234.37
450	220.98	221.72	31596.89	308.34	238.13
475	225.08	224.56	37176.18	320.41	242.14
500	227.28	227.02	42821.61	331.99	246.35
525	228.98	229.17	48524.62	343.12	250.69
550	230.96	231.07	54278.20	353.83	255.14

575	232.02	232.76	60076.58	364.14	259.66
600	232.98	234.28	65914.94	374.08	264.22
625	235.42	235.64	71789.24	383.67	268.81
650	236.08	236.88	77696.03	392.93	273.40
675	237.88	238.01	83632.42	401.90	278.00

Table 3 Standard thermodynamic functions of $Na_2Te_4O_9$ (s).

T K	$C^o_{p,m}$ J K^{-1} mol^{-1}		$H^o_T - H^o_{298.15}$ J mol^{-1}	S^o_T J K^{-1} mol^{-1}	fef J K^{-1} mol^{-1}
	Measured	Fit			
325	316.88	318.69	8331.67	397.99	372.36
350	330.98	331.57	16466.66	422.10	375.05
375	341.24	341.98	24891.25	445.35	378.97
400	350.24	350.51	33551.37	467.70	383.82
425	355.97	357.58	42405.69	489.17	389.39
450	362.89	363.52	51422.04	509.78	395.51
475	367.92	368.55	60575.03	529.58	402.05
500	372.24	372.86	69844.37	548.59	408.90
525	375.89	376.57	79213.60	566.88	415.99
550	380.02	379.79	88669.28	584.47	423.26
575	382.54	382.61	98200.29	601.42	430.64
600	384.92	385.09	107797.37	617.76	438.09
625	387.01	387.28	117452.75	633.52	445.60
650	387.95	389.23	127159.83	648.75	453.12
675	391.32	390.98	136913.02	663.47	460.64

Conclusion

The Na_2TeO_3 (s), $Na_2Te_2O_5$ (s) and $Na_2Te_4O_9$ (s) were synthesized by solid state reaction route and characterized using X-ray powder diffraction method. Standard molar heat capacities of these oxides were determined using DSC in the temperature range of 325-675 K. The specific heats of these oxides were found to follow the trend $Na_2Te_4O_9 > Na_2Te_2O_5 > Na_2TeO_3$. Based on heat capacity measurement, standard thermodynamic functions such as $H^o_T - H^o_{298.15}$, S^o_T and fef were computed. It is essential to generate the enthalpy of formation of these oxides at 298.15 K which can be coupled with heat capacity data obtained in this study to calculate their Gibbs energy of formation in order to explain their relative thermodynamic stabilities.

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