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PREPARATION, CHARACTERIZATION AND STANDARD ENTHALPY OF FORMATION OF Sr_2CeO_4

M. Ali Basu, R. V. Wandekar, S. R. Bharadwaj and D. Das[*]

Applied Chemistry Division, Bhabha Atomic Research Centre, Mumbai 400085, India

Abstract

Sr_2CeO_4 has been prepared by sol-combustion and co-precipitate routes and the resulting products have been characterized by XRD analysis. The molar enthalpies of solution of $Sr_2CeO_4(s)$, $Sr(NO_3)_2(s)$ and $Ce(NO_3)_3\cdot 6H_2O(s)$ in 0.150 dm^3 of (4.41 mol dm^{-3} H_2O_2+4.23 mol dm^{-3} of HNO_3) solvent as well as the molar enthalpies of solution of $Sr_2CeO_4(s)$, $SrCl_2(s)$ and $CeCl_3(s)$ in 0.150 dm^3 of (1.47 mol dm^{-3} H_2O_2+3.05 mol dm^{-3} of $HClO_4$) solvent have been measured using an isoperibol type calorimeter. From these results and other auxiliary data, the standard molar enthalpy of formation of Sr_2CeO_4 has been derived to be –2277.3±3.1 kJ mol^{-1} at 298.15 K. This is the first reported thermodynamic data on this compound.

Keywords: co-precipitation, enthalpy of formation, isoperibol calorimetry, preparation, sol-combustion, Sr_2CeO_4

Introduction

Ceria based solid solutions and compounds find applications in wide ranging areas like oxygen sensors, fuel cells, membrane reactors, inorganic pigments, etc. [1–5]. Some of the ternary compounds such as $SrCeO_3$, $BaCeO_3$, etc. exhibit high proton conductivity when doped with suitable ions and have gained importance in recent years in relation to the development of sensors, electrochromic devices and fuel cells [6–8] and have been extensively investigated. One aspect of such investigation is to study the stability of these materials, especially when they are in contact with gaseous substances. The preparation of these compounds via the usual solid-state synthesis route involves the heating of the mixture of the component oxides at temperatures in the range of 1673 K. An attempt has been made in this work to find some alternative route through which a typical compound like Sr_2CeO_4 could be prepared at a lower temperature, preferably below 1273 K. The compounds prepared by these routes have different microstructures as compared to those prepared by the solid state synthesis route which is reflected in some of their properties like grain boundary and charge transfer resistances [9].

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[*] Author for correspondence: E-mail: dasd@apsara.barc.ernet.in

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Two compounds $SrCeO_3$ and Sr_2CeO_4 are reported in the SrO–CeO_2 system. Thermodynamic data on $SrCeO_3$ is presently available but such data on Sr_2CeO_4 are still lacking. Moreover, Sr_2CeO_4 has some important applications as a luminescent material [10]. In view of this, the enthalpy of formation of Sr_2CeO_4 has been determined by solution calorimetry.

Experimental

The preparation of Sr_2CeO_4 was attempted in the following ways:

a) Sol-combustion route

Sr_2CeO_4 was prepared by sol-gel method through glycine-nitrate route. The chemicals $Ce(NO_3)_3\cdot 6H_2O$ (99.99% purity, Fluka) and $Sr(NO_3)_2$ (99.99% purity, Fluka) were mixed in a molar ratio of 1:2 and a solution was prepared in distilled water. To the above solution, glycine amounting to 2.9 times the number of moles of total metal content was added. This was heated in an open beaker on a hot-plate, at 353 K, until auto-ignition took place. The precursor thus obtained was pelletized and heated, at 1223 K, in air for 48 h.

b) Co-precipitation route

The same compounds, namely cerium and strontium nitrate, as mentioned in ‘a’ above were mixed in a molar ratio of 1:2 and a solution was made in distilled water. The above solution was heated slowly over a hot plate till all the water got evaporated. The resulting pasty mass was heated at 923 K in air till the nitrates got decomposed. The powder thus obtained was dried, ground, pelletized and heated at 1223 K, for 48 h in air.

Sr_2CeO_4 samples resulting from the above mentioned routes were analyzed by XRD. The TG curves were recorded to get the decomposition patterns for ‘a’ the precursors of Sr_2CeO_4 obtained by sol-combustion route and ‘b’ the co-precipitated mixture of strontium and cerium nitrates.

The XRD patterns were recorded in a Philips X-ray generator PW-1729 with wide-angle goniometer PW-1820 using Ni filtered CuK_α radiation. The thermogravimetric runs were taken in a commercial TG-DTA (Setaram, 92-16.18) unit in pure argon atmosphere at a heating rate of 10 K min^{-1}.

The enthalpy of dissolution of $Sr_2CeO_4(s)$ was measured in an isoperibol calorimeter operated at 298.15 K. The construction and operation of the calorimeter is similar to the one described by Athavale *et al*. [11]. The sample was weighed and introduced into a glass bulb which was then thermally equilibrated in the calorimetric solution. The calorimetric solution, i.e., the solvent for the dissolution of Sr_2CeO_4 was 0.150 dm^3 of a 1:1 mixture of 4.41 mol dm^{-3} H_2O_2+4.23 mol dm^{-3} of HNO_3. The glass bulb was broken to introduce the sample into the solution when a steady state signal was obtained on the strip chart recorder. The energy equivalent of the calorimeter was determined before every measurement by electrical calibration. The enthalpies of dissolution of $Sr(NO_3)_2(s)$

and $Ce(NO_3)_3·6H_2O(s)$ were also measured. Using these experimental values and other auxiliary data from literature, the enthalpy of formation of $Sr_2CeO_4(s)$ was determined.

The calorimetric data was also checked using a different solvent consisting of 0.150 dm^3 of a 1:1 mixture of 1.47 mol dm^{-3} H_2O_2+3.05 mol dm^{-3} of $HClO_4$. The enthalpy of dissolution of $Sr_2CeO_4(s)$ was measured in the same way as described in the previous paragraph. The other quantities determined calorimetrically were the enthalpies of dissolution of $SrCl_2(s)$, $CeCl_3(s)$, $HCl(l)$, $H_2O_2(l)$ and $H_2O(l)$. To measure the enthalpies of dissolution of $HCl(l)$, $H_2O_2(l)$ and $H_2O(l)$ 1 mL of the respective solvent was taken in the glass bulb each time and the glass bulb was broken from outside to mix the liquid with the calorimetric solvent and the heat change was recorded as a trace in the recorder.

Results and discussion

The XRD patterns of the compound Sr_2CeO_4 prepared through sol-combustion route and co-precipitation route are presented in Figs 1a and b, respectively. Figures 1a and b are similar and all the peaks present are due to the compound Sr_2CeO_4. The re-

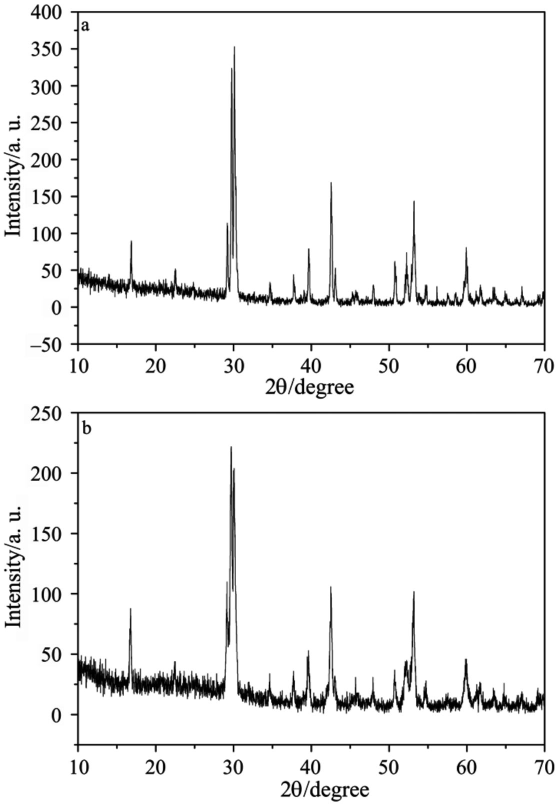

Fig. 1 XRD patterns of Sr_2CeO_4 prepared by a – sol-combustion and b – co-precipitated nitrate routes

corded pattern matched well with that reported in JCPDS file no. 22-1422. The XRD analysis shows that the formation of Sr_2CeO_4 by sol-combustion or co-precipitation route can be achieved at a temperature as low as 1223 K, whereas, solid state reaction route requires heating at 1673 K for 48 h.

Figure 2a shows two distinct steps at 773 and 1123 K out of which the second step might be due to the decomposition of strontium carbonate which gets formed during the process of sol combustion. Figure 2b shows two-step mass loss process corresponding to the decomposition of cerium nitrate and strontium nitrate at 513 and 773 K, respectively.

Sr_2CeO_4 could be synthesized via the solid-state reaction route by heating a 2:1 mixture of $SrCO_3$ and CeO_2 in air at 1673 K for 48 h. Such a high temperature is required because the reaction proceeds through solid-state diffusion mechanism

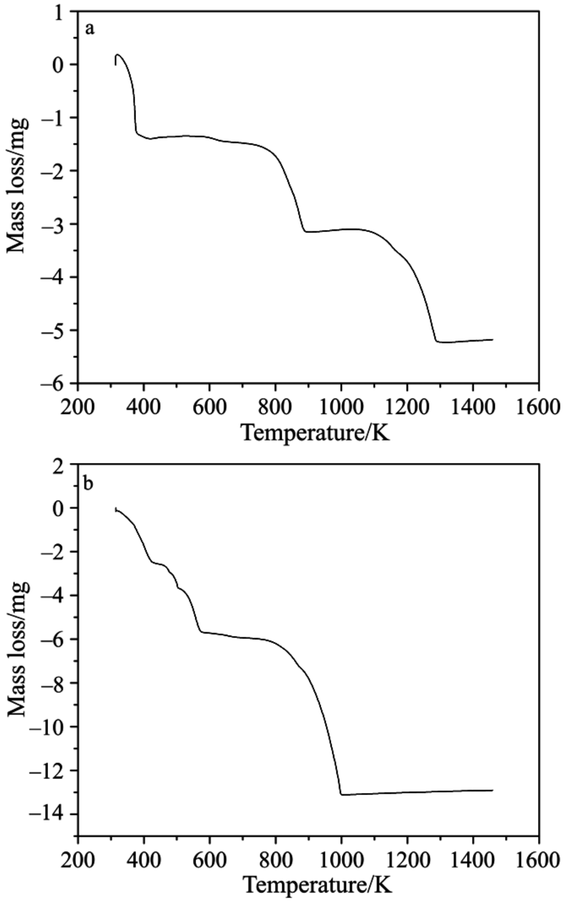

Fig. 2 TG curves showing the decomposition pattern of a – the precursors for Sr_2CeO_4 obtained by a sol-combustion route and b – the co-precipitated mixture of strontium and cerium nitrates

which has a slow kinetics. This part is taken care of in the sol-gel and co-precipitation route by forming a homogeneous mixture of the reactants which facilitates a better reaction kinetics and enable the compound to be formed at a lower temperature (1223 K). In the sol-combustion process the additional factor that initiates the reaction at a lower temperature is the self-ignition of glycine-nitrate couple which increases the local temperature.

The results of the enthalpies of dissolution of $Sr(NO_3)_2(s)$, $Ce(NO_3)_3\cdot 6H_2O(s)$ and $Sr_2CeO_4(s)$ using the HNO_3–H_2O_2 solvent system are given in Table 1. Here m denotes the mass of the sample dissolved, ΔH is the measured energy change and $\Delta_{sol}H_m$ is the molar enthalpy of dissolution. The thermochemical cycle from which the standard molar enthalpy of formation of Sr_2CeO_4 has been derived is given in Table 2. Table 3 tabulates the enthalpy of dissolution of $Sr_2CeO_4(s)$, $SrCl_2(s)$ and $CeCl_3(s)$ using $HClO_4$–H_2O_2 as the solvent. The quantities m and ΔH have the same significance. The corresponding thermochemical cycle is given in Table 4.

The experimentally measured values obtained using the HNO_3–H_2O_2 combination as the solvent have been combined with other auxiliary data such as the standard enthalpies of formation of $Sr(NO_3)_2(s)$ [12], $Ce(NO_3)_3\cdot 6H_2O(s)$ [13], $HNO_3(l)$ [13], $H_2O(l)$ [14] and $H_2O_2(l)$ [15] to derive the standard molar enthalpy of formation of $Sr_2CeO_4(s)$ at 298.15 K which works out to be –2278.3±2.9 kJ mol^{-1}. The other cycle considered was the one using $HClO_4$–H_2O_2 combination as the solvent. The experimentally measured values were the enthalpies of dissolution of $Sr_2CeO_4(s)$, $SrCl_2(s)$, $CeCl_3(s)$, $HCl(l)$, $H_2O_2(l)$ and $H_2O(l)$. The enthalpies of dissolution for $HCl(l)$, $H_2O_2(l)$ and $H_2O(l)$ were negligible and no significant signal could be obtained. In spite of that these steps are shown in the thermochemical cycle

Table 1 The molar enthalpies of dissolution of $Sr_2CeO_4(s)$, $Sr(NO_3)_2(s)$ and $Ce(NO_3)_3\cdot 6H_2O(s)$ in 0.150 dm^3 of (4.41 mol dm^{-3} H_2O_2+4.23 mol dm^{-3} of HNO_3) at T=298.15 K; m denotes the mass of the sample dissolved; ΔH is the measured energy change and $\Delta_{sol}H_m$ is the molar enthalpy of solution

Solute	m(solute)/g	ΔH/J	$\Delta_{sol}H_m$/kJ mol^{-1}
$Sr_2CeO_4(s)$ mol. mass=379.36	0.0425	–65.37	–583.46
	0.0722	–111.04	–583.44
	0.1021	–157.27	–584.33
	0.0787	–120.92	–582.88
			Av. –583.53±0.60
$Sr(NO_3)_2(s)$ mol. mass=211.62	1.1969	67.93	12.01
	0.9991	56.28	11.92
	1.4110	86.75	13.01
	1.9220	108.81	11.98
			Av. 12.23±0.52
$Ce(NO_3)_3\cdot 6H_2O(s)$ mol. mass=434.12	1.0117	49.17	21.10
	1.1534	64.30	24.20
	0.8637	49.48	24.87
	0.6589	36.53	24.07
			Av. 23.56±1.68

Table 2 Reaction scheme for the standard molar enthalpy of formation of $Sr_2CeO_4(s)$ (sln=0.150 dm^3 of 4.41 mol dm^{-3} H_2O_2+4.23 mol dm^{-3} of HNO_3) $\Delta H_{10}=-\Delta H_1+\Delta H_2+\Delta H_3+\Delta H_4+\Delta H_5+\Delta H_6+\Delta H_7+\Delta H_8+\Delta H_9$

Reaction	ΔH_m/kJ mol^{-1}
$2Sr_2CeO_4(s)+[14HNO_3+H_2O_2](sln)=$ $[4Sr(NO_3)_2+2Ce(NO_3)_3](sln)+8H_2O(sln)+O_2(g)$	–1167.06±1.20
$4Sr(NO_3)_2(s)+sln=4Sr(NO_3)_2(sln)$	48.92±2.08
$2Ce(NO_3)_3\cdot 6H_2O(s)+sln=2Ce(NO_3)_3(sln)+12H_2O(l)$	47.12±3.36
$2Ce(s)+3N_2(g)+9O_2(g)=2Ce(NO_3)_3(s)$	–2449.40±2.12
$2Ce(NO_3)_3(s)+12H_2O(l)=2Ce(NO_3)_3\cdot 6H_2O(s)$	–216.17±0.53
$14HNO_3(sln)=7H_2(g)+7N_2(g)+21O_2(g)$	2853.76±1.17
$4Sr(s)+4N_2(g)+12O_2(g)=4Sr(NO_3)_2(s)$	–3912.48±3.24
$H_2O_2(sln)=H_2(g)+O_2(g)$	190.95±0.85
$8H_2(g)+4O_2(g)=8H_2O(sln)$	–2286.40±0.04
$4Sr(s)+2Ce(s)+4O_2(g)=2Sr_2CeO_4(s)$	–4556.64±5.87

Table 3 The molar enthalpy of dissolution of $Sr_2CeO_4(s)$ in 0.150 dm^3 of (1.47 mol dm^{-3} H_2O_2+3.05 mol dm^{-3} of $HClO_4$) at T=298.15 K; m denotes the mass of the sample dissolved; ΔH is the measured energy change and $\Delta_{sol}H_m$ is the molar enthalpy of solution

Solute	m(solute)/g	ΔH/J	$\Delta_{sol}H_m$/kJ mol^{-1}
$Sr_2CeO_4(s)$ mol. mass=379.36	0.0956	–140.88	–559.03
	0.0490	–72.52	–561.48
	0.0438	–65.07	–563.57
	0.0301	–44.50	–560.83
			Av. –561.23±1.87
$CeCl_3(s)$ mol. mass=246.6	0.1506	–85.02	–139.21
	0.2197	–125.47	–140.84
	0.2214	–128.04	–142.61
	0.2261	–130.60	–142.44
			Av. –141.27±1.59
$SrCl_2(s)$ mol. mass=158.52	0.1417	–41.22	–46.11
	0.1511	–45.10	–47.31
	0.0876	–25.61	–46.34
	0.1086	–31.91	–46.58
			Av. –46.58±0.52

to maintain the proper mass balance, assuming that for these steps there have been negligible heat change. With these values and other auxiliary data such as the standard enthalpies of formation of $SrCl_2(s)$ [16], $CeCl_3(s)$ [17], $HCl(l)$ [18], $H_2O(l)$ [14] and $H_2O_2(l)$ [15] were combined to derive the standard molar enthalpy of formation of $Sr_2CeO_4(s)$ at 298.15 K as –2276.2±3.2 kJ mol^{-1}. The molar enthalpies of dissolution for the compounds $Sr_2CeO_4(s)$, $SrCl_2(s)$, $CeCl_3(s)$, $Sr(NO_3)_2(s)$ and

Table 4 Reaction scheme for the standard molar enthalpy of formation of Sr_2CeO_4 (sln=0.150 dm^3 of 1.47 mol dm^{-3} H_2O_2+3.05 mol dm^{-3} of $HClO_4$)
$\Delta H_{12}=-\Delta H_1+\Delta H_2+\Delta H_3+\Delta H_4+\Delta H_5-\Delta H_6-\Delta H_7+\Delta H_8+\Delta H_9-\Delta H_{10}-\Delta H_{11}$

Reaction	ΔH_m/kJ mol^{-1}
$2Sr_2CeO_4(s)+[14HClO_4+H_2O_2](sln)=$ $[4Sr(ClO_4)_2+2Ce(ClO_4)_3](sln)+8H_2O(sln)+O_2(g)$	–1122.46±3.74
$4SrCl_2(s)+[8HClO_4+0.571H_2O_2](sln)=$ $4Sr(ClO_4)_2(sln)+8HCl(sln)+0.571H_2O_2(sln)$	–186.33±2.08
$2CeCl_3(s)+[6HClO_4+0.429H_2O_2](sln)=$ $2Ce(ClO_4)_3(sln)+6HCl(sln)+0.429H_2O_2(sln)$	–282.54±3.18
$4Sr(s)+4Cl_2(s)=4SrCl_2(s)$	–3329.72±3.40
$2Ce(s)+3Cl_2(g)=2CeCl_3(s)$	–2121.08±1.06
$14HCl(l)+sln=14HCl(sln)^*$	0.00
$7H_2(g)+7Cl_2(g)=14HCl(l)$	–2340.20±0.04
$8H_2O(l)+sln=8H_2O(sln)^*$	0.00
$8H_2(g)+4O_2(g)=8H_2O(l)$	–2286.40±0.04
$H_2O_2(l)+sln=H_2O_2(sln)$	–0.04±0.04
$H_2(g)+O_2(g)=H_2O_2(l)$	–190.95±0.85
$4Sr(s)+2Ce(s)+4O_2(g)=2Sr_2CeO_4(s)$	–4552.42±6.47

The enthalpy changes marked with '' in above Table 4 were negligible and were below the detection limit of our calorimeter. But these steps have been included in the cycle to maintain the proper mass balance

$Ce(NO_3)_3\cdot 6H_2O$ (s) are seen to vary randomly with the molar concentration of these compounds. This indicates that there was no dilution effect and in each case the experiments were carried out in infinite dilution condition. So in each case the average of four values is taken. It is seen that the agreement between the two values obtained through two different thermochemical routes is quite good.

The stabilization energy of a double oxide can be defined as the enthalpy change for its formation from the constituent binary oxides. For the spinels (A_2BO_4) this can be written as δ_k (A_2BO_4)=$\Delta_f H°$ (A_2BO_4)–[$2\Delta_f H°$ (AO)+$\Delta_f H°$ (BO_2)] where δ_k is the enthalpy of formation from the oxides. A linear correlation between the stabilization energy and Goldschmidt's tolerance factor t is found to exist: $\delta_k=3[-65+400(1-t)]$ for spinels [19]. The parameter t is defined as $t=(r_A+r_O)/\sqrt{2(r_B+r_O)}$ where r_O is the ionic radius of oxygen ion and r_B is the Shannon radius for B-site ion with 6 coordination and r_A the Shannon radius of the A site ion. Shannon radii for the coordination number 9 was adopted for the spinel compound. The value of t was computed to be 0.8442 for Sr_2CeO_4. The stabilization energy was estimated to be –8.04 kJ mol^{-1} from the linear correlation equation whereas the nitric acid–peroxide cycle gave the value as –6.32 kJ mol^{-1} and the perchloric acid–peroxide cycle gave the value as –4.23 kJ mol^{-1}. It is seen that the agreement is quite good.

Conclusions

The compound Sr_2CeO_4 could be prepared at a low temperature of 1223 K by adopting sol-combustion or co-precipitation routes. The standard enthalpy of formation of the compound at 298.15 K is found to be –2277.3±3.1 kJ mol^{-1}. This is the first experimental thermodynamic data reported for Sr_2CeO_4.

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