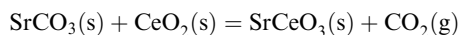# Thermodynamic stability of SrCeO$_3$

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Abstract

Thermochemistry of the reaction between SrCO$_3$ and CeO$_2$ as

$$SrCO_3(s) + CeO_2(s) = SrCeO_3(s) + CO_2(g)$$

was studied over the temperature range 1113–1184 K. The equilibrium pressure of CO$_2$(g) over the ternary phase mixture of SrCO$_3$(s), CeO$_2$(s) and SrCeO$_3$(s) was measured at various temperatures using a tensimetric apparatus. The temperature dependence of the measured CO$_2$(g) pressure could be represented as

$$\text{Log} \, (p_{CO_2} \, (\text{Pa})) \, (\pm 0.04) = -11534(\pm 750)/T + 13.1(\pm 0.7), \quad (1113 \leqslant T \, (\text{K}) \leqslant 1184).$$

Tensimetric measurements were also carried out for the decomposition of SrCO$_3$(s). The equilibrium vapor pressures of CO$_2$(g) over the biphasic mixture of SrCO$_3$(s) and SrO(s) could be represented as

$$\text{Log} \, p_{CO_2} \, (\text{Pa}) \, (\pm 0.01) = -11139(\pm 263)/T + 12.72(\pm 0.2), \quad (1045 \leqslant T \, (\text{K}) \leqslant 1123).$$

The observed CO$_2$ pressures were compared with those obtained for reaction (1). Simultaneous thermogravimetric/differential thermal analysis experiments were carried out for reaction (1) and for the decomposition of SrCO$_3$ in CO$_2$ atmospheres. All these results were used to derive the thermodynamic properties of SrCO$_3$(s) and SrCeO$_3$(s).
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1. Introduction

Perovskite-type ternary oxides such as BaCeO$_3$ and SrCeO$_3$ are important materials in various fields of technology. They have potential applications in hydrogen-based fuel cells, hydrogen extractors from gas mixtures, and in high-temperature hydrogen sensors [1–4] because they exhibit high protonic conductivity when doped with rare-earth elements. Typically, their conductivities in hydrogen atmosphere are of the order of 10^{-2}–10^{-3} S cm^{-1} at 1273–873 K [5]. In the above-mentioned applications, the exposure of these electrochemical materials to gaseous atmosphere containing CO$_2$(g) impurity, could be detrimental to their performance. At normal pressure of CO$_2$(g), the cerates could react forming alkaline earth carbonates [6–8]. In order to evaluate the chemical compatibility of the cerates

with CO$_2$ impurity, it is necessary to have knowledge of thermodynamic properties of these compounds with respect to the corresponding alkaline earth carbonates (MCO$_3$, M = Sr or Ba). In this context, the present study looked into reported thermochemistry of SrCeO$_3$(s) and SrCO$_3$(s) [6,7,9,10] and found that there is need for reliable data acquisition on the properties since the available data suffer from inconsistencies. The reported observation that SrCeO$_3$(s) is thermodynamically unstable with respect to the constituent oxide SrO(s) and CeO$_2$(s) [7] could not be explained by the calorimetrically measured data of standard enthalpy and entropy of formation [9,11] of SrCeO$_3$(s). Standard Gibbs free energy of formation of SrCeO$_3$(s) obtained from galvanic cell measurement [7] does not corroborate to the calorimetric data [9,11]. Further, the reported thermogravimetric (TG) results [6,12] for SrCeO$_3$(s) formation from SrCO$_3$(s) and CeO$_2$(s) mixture under controlled CO$_2$(g) pressures indicated poor agreements between the thermodynamically assessed and the observed onset

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temperatures of the following reaction:

$$SrCO_3(s) + CeO_2(s) = SrCeO_3(s) + CO_2(g). \qquad (1)$$

Similarly, the available stability data of $SrCO_3(s)$ [13] inadequately predict the reported TG results for onset temperatures of the carbonate decomposition at different partial pressures of $CO_2(g)$ [6,12,14]. It is also inconsistent with the manometric results [15] of the decomposition to be represented as

$$SrCO_3(s) = SrO(s) + CO_2(g). \qquad (2)$$
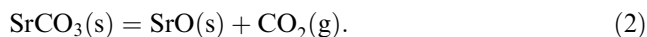
In this study, the thermodynamic stabilities of $SrCeO_3(s)$ and $SrCO_3(s)$ have been determined by tensimetric measurement of the equilibrium $CO_2(g)$ pressures of reactions (1) and (2), respectively. To complement the tensimetric data acquisition, TG studies on the reaction between $SrCO_3(s)$ and $CeO_2(s)$ (1:1 mole ratio) and also on the decomposition of $SrCO_3(s)$ were carried out in controlled CO_2 atmospheres. The tensimetric and TG results were consolidated to derive the thermodynamic stabilities of $SrCeO_3(s)$ and $SrCO_3$. The results of these studies are discussed in the light of the available thermochemical data of the two compounds.

2. Experimental

$SrCeO_3(s)$ was prepared by mixing $SrCO_3(s)$ (99.99%, Alfa Aesar, USA) and $CeO_2(s)$ (99.9%, Indian Rare Earths Ltd.) in stoichiometric amounts and heating the sample at 1173 K for 4 h followed by heating at 1673 K for 48 h in air with intermittent grinding. The XRD pattern of the product was indexed and matched with JC-PDS file No. 23–1412 for $SrCeO_3$.

TG and differential thermal analysis (DTA) studies were carried out using a simultaneous TG-DTA apparatus (SETARAM 92-16.18), France) on 1:1 mixture of $SrCO_3 + CeO_2$ and on pure $SrCO_3$ samples in flowing CO_2 gas, and, in CO_2 and argon gas mixtures in different proportions at a heating rate of $5 \, K \, min^{-1}$. The weight loss characteristics and other thermal effects were noted at different partial pressures of $CO_2(g)$ in both the cases. The recorded temperature scale of the TG profiles was precalibrated by noting the melting temperatures of pure silver and gold.

For tensimetric study of reaction (1), the ternary mixture of $SrCO_3(s)$ $CeO_2(s)$ and $SrCeO_3(s)$ and for reaction (2) the biphasic mixture of $SrCO_3(s)$ and $SrO(s)$ were used as samples. Typically, 500 mg powder sample taken in each of the cases in a platinum boat was located inside uniform temperature zone of a one end closed quartz reaction tube inserted in a horizontal resistance furnace, which was equipped with controlled heating facility. The other end of the reaction tube could be coupled to an oil manometer or to a mercury manometer both of which were connected with gas tight joints. The manometer of di-butyl phthalate oil could measure pressure up to 7500 Pa with readability of 5 Pa. The manometers were made out of pyrex glass to render readabilities of their fluid levels. The dead volume of the system, i.e., the quartz reaction tube together with the connecting limbs of the two manometers, was less than 25 mL. The system was coupled to a high vacuum system through quick fit stopcock and could hold static vacuum over several weeks to better than the measuring sensitivity of the oil manometer. Sample temperature was measured with the help of a Pt–Pt13%Rh thermocouple which was calibrated at the melting points of pure metals as recommended in Ref. [16]. The temperature could be measured to an accuracy of ± 1 K.

After loading the sample in the tensimetric apparatus, the system was evacuated under the dynamic vacuum of 1×10^{-3} Pa. Under evacuation, the sample temperature was raised to 773 K to let off any absorbed moisture from the sample. The conditioning was continued till the static pressure of the system measured by the oil manometer became constant. The system was then isolated from the vacuum pump for taking measurements. The chemical paths of reactions (1) and (2) were established by TG analysis and by recording the XRD patterns of residual samples after the pressure measurements. The phase equilibria involved in reaction (2) was also established by high-temperature XRD analysis of the condensed phases during the decomposition of $SrCO_3(s)$.

As the system for reactions (1) or (2) was thermally cycled around a fixed temperature and the course of development or recession of CO_2 pressure were monitored, it was seen that the fluid level in the manometer ultimately converged to a constant value. It was also seen that the gas pressure developed in the respective closed systems when relieved temporarily, developed back to the same value at any fixed sample temperature. The attainment of pressure invariancy at a temperature following the thermal and mechanical perturbations was indicative of reversibility and accomplishment of thermodynamic equilibrium in each of the reactions. The lower and upper limits of temperature for the measurements involving reactions (1) and (2) were within 1113–1184, and 1045–1123, respectively. The working temperature limits were primarily governed by the slow kinetics of attainment of equilibrium CO_2 pressure for a given surface to volume ratio of sample. Fast sintering of the condensed phases involved in the respective cases was responsible for slowing down of reaction kinetics at higher temperature limits.

3. Results and discussion

The XRD pattern for $SrCeO_3(s)$ prepared in this study could be indexed based on an orthorhombic

symmetry with the following lattice parameters: $a = 0.8570(2)$ nm, $b = 0.5997(2)$ nm and $c = 0.6142(1)$ nm. The typical TG-DTA profiles for $CeO_2(s) + SrCO_3(s)$ mixture and for pure $SrCO_3(s)$ observed at 1 bar (1 bar = 101333 Pa) pressure of $CO_2(g)$ are given in Figs. 1 and 2, respectively. In Fig. 1 as well as Fig. 2, it is seen that before the onset of reactions (1) and (2) there is an endotherm at 1195 ± 1 K of the reported orthorhombic to rhombohedral phase transition of $SrCO_3(s)$ [13]. The characteristic temperatures of weight losses due to reactions (1) and (2) under different $CO_2(g)$ partial pressures are included in Table 1. The recorded HTXRD pattern for the decomposition of $SrCO_3(s)$ at 1073 K in nitrogen is indicated in Fig. 3. The figure also includes the XRD pattern of pure $SrCO_3(s)$ for comparison. Attainment of pressure invariancy at set temperatures for reactions (1) and (2) are typically shown in Figs. 4 and 5, respectively.
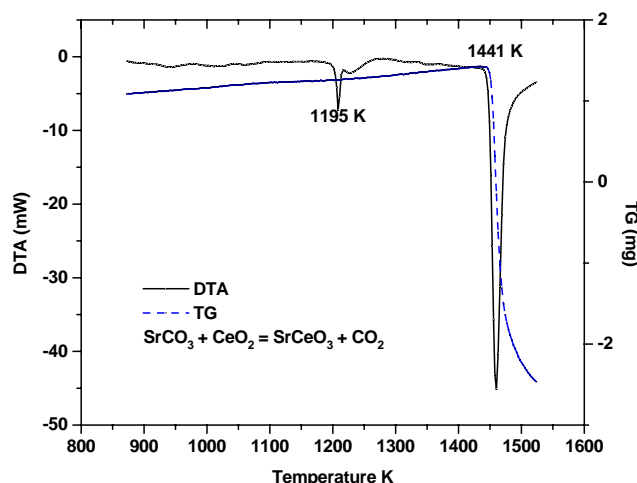

Fig. 1. TG-DTA curves for the reaction $SrCO_3(s) + CeO_2(s) = SrCeO_3(s) + CO_2(g)$ in 1 bar (1 bar = 101,333 Pa) pressure of CO_2.
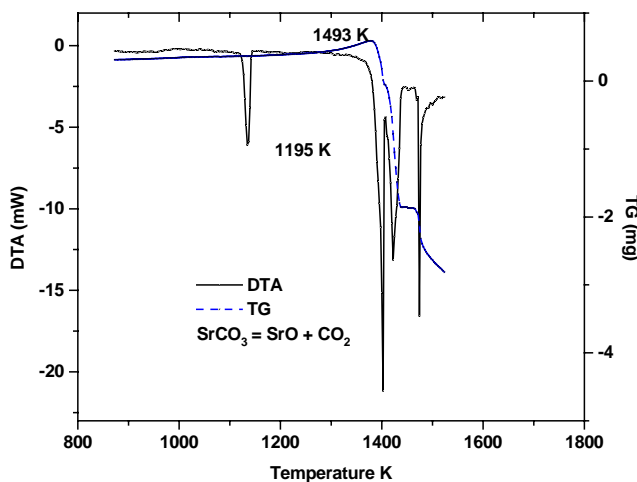
Fig. 2. TG-DTA curves for the reaction $SrCO_3(s) = SrO(s) + CO_2(g)$ in 1 bar (1 bar = 101333 Pa) pressure of CO_2.

The equilibrium pressures of $CO_2(g)$ for reactions (1) and (2) monitored at different set temperatures of the tensimetric experiments are included in Table 1. Each of the pressure readings given in the table is actually the average value of several readings taken at large time intervals as the system attained equilibrium at a temperature typically within half a day to a few days depending on the temperature. This averaging was done to even out the effect of room temperature fluctuation on the manometric readings. It may be noted that the room temperature fluctuated within ± 2 K, which corresponded to an insignificantly small uncertainty in the recorded height of dibutyl phthalate oil (sp. gravity 1.045 at 293 K), used. Table 1 also includes the tensimetric results of the onset temperatures for reactions (1) and (2) at different CO_2 pressures.

The tabulated tensimetric data over the triphasic mixture of $SrCO_3(s)$, $CeO_2(s)$ and $SrCeO_3(s)$ at various temperatures could be represented as

$$\text{Log}(p_{CO_2}(\text{Pa})) \, (\pm 0.04) = -11534(\pm 750)/T \\ + 13.1(\pm 0.7), \quad (1113 \leqslant T(\text{K}) \leqslant 1184). \quad (3)$$

The corresponding plot of $\text{Log}\, p_{CO_2}$ as a function of $1/T$ is given in Fig. 6. In order to compare the results of tensimetry with those obtained in TG study, Eq. (3) was extrapolated to higher temperatures above the ortho-rhombic to rhombohedral phase transition of $SrCO_3(s)$ at 1195 ± 1 K. Above 1195 K, the extrapolation with appropriate correction of the slope and intercept, respectively, by the reported values of standard enthalpy (19.665 kJ mol^{-1}) and entropy (16.429 J K^{-1} mol^{-1}) of the phase transformation [13] led to the equation: $\text{Log}(p_{CO_2}(\text{Pa})) \, (\pm 0.04) = -10507 \, (\pm 750)/T + 12.24 \, (\pm 0.7)$. The extrapolation made the implicit assumption that standard enthalpy and entropy of reaction (1) remain constant all through the extrapolated region of temperatures. The arrived equation can be well compared with the linear fitting, $\text{Log}(p_{CO_2}(\text{Pa})) \, (\pm 0.01) = -10529 \, (\pm 278)/T + 12.31 \, (\pm 0.2)$, obtained from the pressure–temperature data of TG experiments for the onset temperatures of reaction (1) at different partial pressures of $CO_2(g)$ (Table 1). The observed onset temperature of 1441 ± 10 K under 1 bar pressure of $CO_2(g)$ compares reasonably with the decomposition temperature of 1452 ± 10 K obtainable from the extrapolated equation of (3). In the extrapolation of Eq. (3) when the corrections of slope and intercept were made for the heat capacity difference of products and reactants of reaction (1) in addition to the enthalpy and entropy change of the phase transition of $SrCO_3$ at 1195 K, the extrapolation showed that one bar p_{CO_2} is attained at 1460 K. The required heat capacity data for this exercise were taken from the available literatures [9,13].

To derive the thermodynamic stability for $SrCeO_3(s)$ from the CO_2 partial pressures expressed in Eq. (3), it is

Table 1
Equilibrium pressures of CO_2(g) measured over the triphasic mixture of $SrCO_3$(s), CeO_2(s) and $SrCeO_3$(s) and biphasic mixture of $SrCO_3$(s) and SrO(s) as functions of temperature

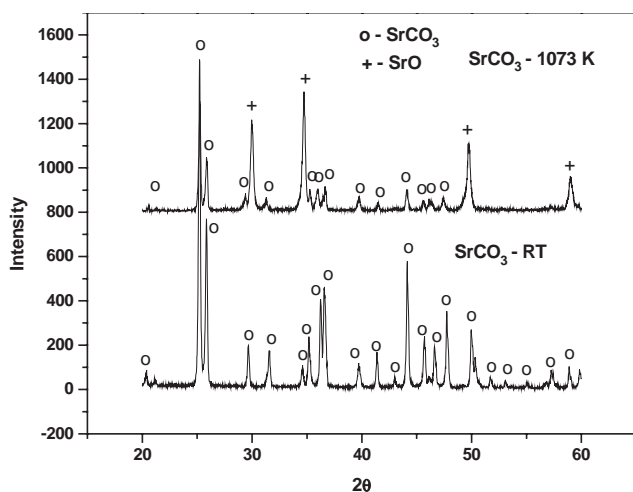| Type of experiment	Temperature T (K)	p_{CO_2} ($SrCO_3 + CeO_2$) (Pa)	Temperature T (K)	p_{CO_2} ($SrCO_3$) (Pa)
Manometry	1113	502	1045	112
	1118	717	1057	149
	1126	706	1077	252
	1127	666	1089	327
	1143	1147	1098	383
	1148	1117	1110	467
	1160	1312	1115	533
	1163	1681	1123	626
	1178	2130	1147	842
	1184	2171		
TG/DTA	1299	16,284	1368	24,096
	1343	28,636	1427	45,700
	1441	101,331	1493	101,331

Fig. 3. High-temperature XRD patterns taken during the decomposition of $SrCO_3$(s) at 1073 K in vacuum (room temperature pattern is also given for comparison).
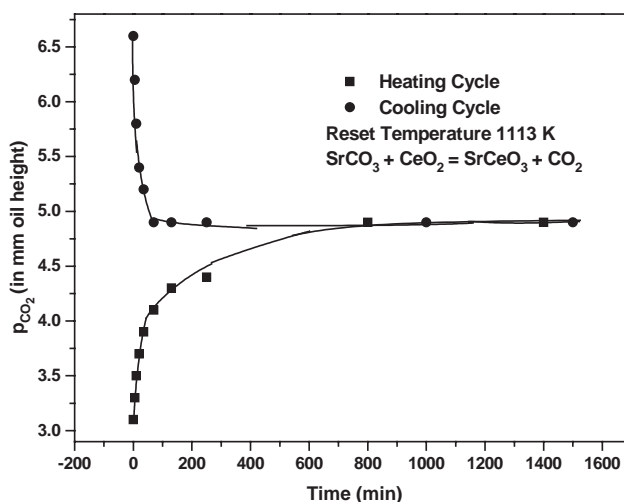

Fig. 4. The invariancy of equilibrium pressure at 1113 K as the sample is thermally cycled around this temperature for the reaction, $SrCO_3$(s) + CeO_2(s) = $SrCeO_3$(s) + CO_2(g).

necessary to have the stability data of other compounds involved in reaction (1). The stability of $SrCeO_3$(s) could be expressed as

$$\Delta_f G^0(SrCeO_3(s)) = \Delta_f G^0(SrCO_3(s)) + \Delta_f G^0(CeO_2(s)) \\ - \Delta_f G^0(CO_2(g)) - RT \ln(p_{CO_2}(bar)). \quad (4)$$

The available thermodynamic data on $SrCO_3$(s) [13] were seen to be inconsistent with tensimetric and TG-DTA of this study as well as other studies [6,12,14,15]. The equilibrium CO_2(g) pressures for the decomposition calculated as a function of temperature using the compiled thermodynamic data for $SrCO_3$(s), SrO(s) and CO_2(g) [13] indicates that $SrCO_3$(s) should decompose at 1426 ± 10 K in 1 bar pressure of CO_2(g). The calculated result is in contrast with the decomposition

temperature of 1493 ± 15 K observed in the present TG study (Fig. 2). The reported TG and tensimetric studies give still higher values 1515–1548 K for the decomposition temperature [6,12,14,15]. In Fig. 2, the additional DTA peaks and TG steps seen following the onset of decomposition could be explained from reported phase equilibrium studies on the SrO–CO_2 system [14]. Baker [14] reported that above 1543 K and 1.12 bar, the dissociation of $SrCO_3$ is accompanied by fusion of the resultant oxide with unchanged carbonate to form melts. In view of the TG result, the reported data of $\Delta_f G^0$ ($SrCO_3$(s)) [13] could not be used for deriving $\Delta_f G^0$ ($SrCeO_3$(s)) from Eq. (4). The tensimetric data of reaction (2) obtained in this study was instead used to derive $\Delta_f G^0$ ($SrCeO_3$(s)) as it could well account for the TG results.
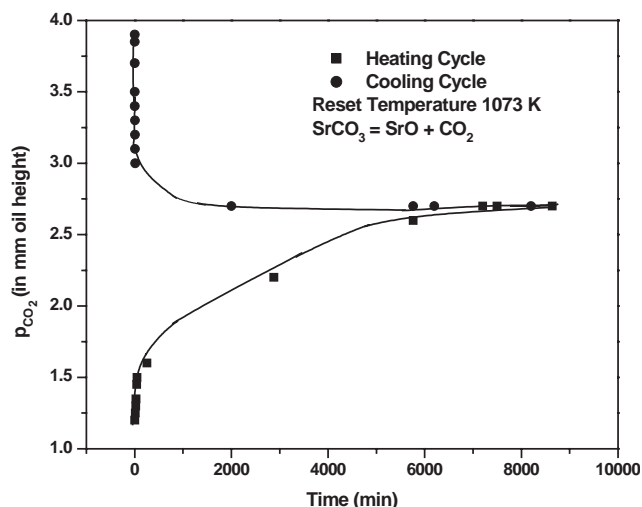
Fig. 5. The invariancy of equilibrium pressure at 1073 K as the sample is thermally cycled around this temperature for the reaction, $SrCO_3(s) = SrO(s) + CO_2(g)$.

Fig. 7. Inter-comparison of present and reported results of manometric and TG studies on the reactions, $SrCO_3(s) = SrO(s) + CO_2(g)$ and $SrCO_3(s) + CeO_2(s) = SrCeO_3(s) + CO_2(g)$.
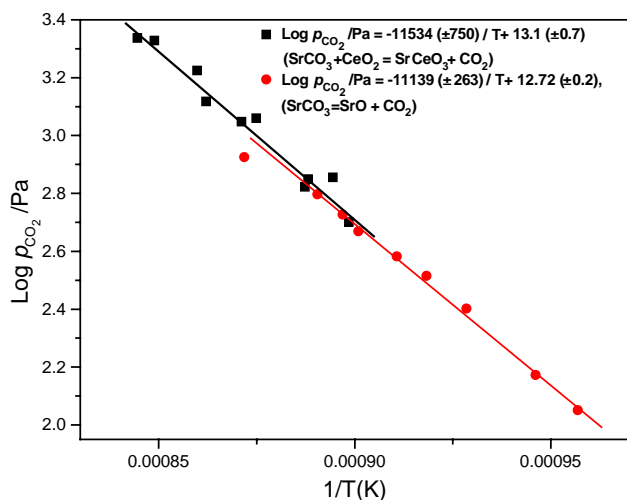

Fig. 6. Plot of $Log(p_{CO_2} (Pa))$ as a function of reciprocal temperature for the two reactions, $SrCO_3(s) + CeO_2(s) = SrCeO_3(s) + CO_2(g)$ and $SrCO_3(s) = SrO(s) + CO_2(g)$.

The tensimetric data in Table 1 on equilibrium vapor pressures of $CO_2(g)$ over the biphasic mixture of $SrCO_3(s)$ and $SrO(s)$ are graphically shown as $Log\, p_{CO_2}$ versus $1/T$ plot in Fig. 6. It may be noted in the plot that p_{CO_2} data at the highest temperature, 1147 K (Table 1) deviates significantly from the linear trend established by the rest of the vapor pressure data. The negative deviation seen at this and at still higher temperatures (not included in the table) were due to extremely slow release of $CO_2(g)$ for attaining the manometric equilibrium. The tabulated highest temperature data was excluded from linear regression analysis of the other data set that resulted in the
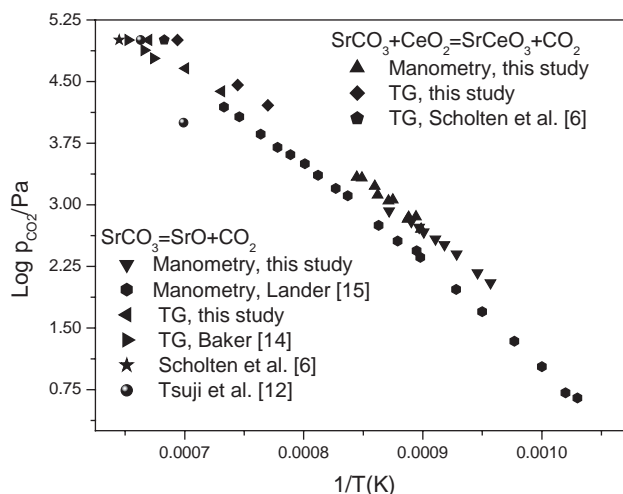
following equation:

$$Log\, p_{CO_2}(Pa)\,(\pm 0.01) = -11139(\pm 263)/T + 12.72(\pm 0.2), \quad (1045 \leqslant T(K) \leqslant 1123). \tag{5}$$

The tensimetric and TG results of this study are compared with the reported results [15] in Fig. 7. The manometrically measured p_{CO_2} data of Lander [15] are systematically lower from the present data. The reported p_{CO_2} [15] values are approximately half the values of the reversibly measured equilibrium pressures of this study. The p_{CO_2} data obtainable from the compiled thermodynamic properties of Barin [13] are comparatively closure to the presently obtained data; the values from compilation are systematically higher by 20%.

Like the case of reaction (1) the tensimetric results of reaction (2) were compared with those obtained in the present TG study. Eq. (5) was extrapolated to temperatures above the orthorhombic to rhombohedral phase transition of $SrCO_3(s)$ at 1195 ± 1 K by making at first correction of the slope and intercept, respectively, by the reported values of standard enthalpy and entropy of the phase transformation of $SrCO_3(s)$ [13]. The extrapolated equation could be written as $Log(p_{CO_2}(Pa))\,(\pm 0.01) = -10112(\pm 263)/T + 11.84(\pm 0.2), \quad (1195 \leqslant T(K))$. The arrived equation can be well compared with the linear fitting, $Log(p_{CO_2}(Pa))\,(\pm 0.01) = -10200(\pm 564)/T + 11.82(\pm 0.2)$, obtained from the pressure–temperature data of TG experiments for the onset temperatures of reaction (2) at different partial pressures of $CO_2(g)$ (Table 1). The onset temperature of 1493 ± 15 K observed under 1 bar pressure of $CO_2(g)$ can be compared with the decomposition temperature of 1476 ± 10 K obtainable from the linearly extrapolated equation of (5). In the extrapolation of Eq. (5) when the corrections of slope and intercept were made for the heat capacity difference of

products and reactants of reaction (2) in addition to the enthalpy and entropy change of the phase transition of $SrCO_3$ at 1195 K, the extrapolation showed that 1 bar p_{CO_2} is attained at 1503 K. The required heat capacity data for this exercise were taken from the compilation of Barin [13]. It is to be noted that the reported TG and manometric data [6,12,14,15] give higher onset temperatures for $SrCO_3$ decomposition at 1 bar pressure of CO_2. The higher temperatures could be due to higher heating rates used in the TG studies [6,12].

The standard free energy of formation of $SrCO_3(s)$ obtained from Eq. (5) along with other auxiliary data [13] on $SrO(s)$ and $CO_2(g)$ could be expressed as

$$\Delta_f G^0(SrCO_3(s))\,(\pm 5.0\,kJ\,mol^{-1}) = -1206 + 0.25\,T$$
$$(1045 \leqslant T(K) \leqslant 1123). \qquad (6)$$

The thermodynamic stability data of $SrO(s)$ and $CO_2(g)$ taken from the compilation [13] and used in deriving Eq. (6) could be represented as $\Delta_f G^0\,(SrO(s))$ $(\pm 0.11\,kJ\,mol^{-1})\quad = -596.53 + 0.105T,\quad$ and $\quad \Delta_f G^0$ $(CO_2(g))\,(\pm 0.01\,kJ\,mol^{-1}) = -394.92 - 8.96 \times 10^{-4}T.$

The result given in Eq. (6) is to be compared with that obtainable from the reported (i) manometric data of Lander [15] as $\Delta_f G^0\,(SrCO_3(s))\,(\pm 5.0\,kJ\,mol^{-1}) = -1238 + 0.27T,\,(969 \leqslant T(K) \leqslant 1158),$ and (ii) thermodynamic data compilation of Barin [13] as $\Delta_f G^0$ $(SrCO_3(s)) = -1218.6 + 0.266T.$ From the compilation [13], the $\Delta_f G^0$ equation was derived in the temperature range of $(1000 \leqslant T\,(K) \leqslant 1150)$. The second law enthalpy and entropy of formation of $SrCO_3(s)$ seen in Eq. (6) and in the derived equation from the compilation are in fair agreement. It is to be noted here that the result presented in Eq. (6) was derived from the reversibly measured equilibrium pressure of CO_2 in reaction (2), and therefore this result should be more reliable than the others.

The Gibbs energy of $SrCeO_3(s)$ derived from the results of this study, i.e., from Eqs. (3), (4) and (6) and from the available thermodynamic data [13] on $CeO_2(s)$ and $CO_2(g)$ is given by

$$\Delta_f G^0(SrCeO_3(s))\,(\pm 7.0\,kJ\,mol^{-1}) = -1680.5 + 0.31\,T$$
$$(1113 \leqslant T\,(K) \leqslant 1184). \qquad (7)$$

In deriving Eq. (7), the stability data of $CeO_2(s)$ and $CO_2(g)$ taken from the compilation [13] and used therein could be represented as $\Delta_f G^0\,(CeO_2(s))$ $(\pm 0.4\,kJ\,mol^{-1}) = -1085.7 + 0.20T,$ and $\Delta_f G^0\,(CO_2(g))$ $(\pm 0.01\,kJ\,mol^{-1})\ = -394.92 - 8.96 \times 10^{-4}\,T.$

The values of standard enthalpy and entropy of formation of $SrCeO_3(s)$ obtained from (7) at the mean temperature of 1150 K of this study are, respectively, $-1680.5 \pm 10.0\,kJ\,mol^{-1}$ and $-310 \pm 10.0\,J\,mol^{-1}\,K^{-1}$. Cordfunke et al. [9] have reported the enthalpy of formation of $SrCeO_3(s)$ from solution calorimetry and also, reported heat capacity measurements on this

compound. The standard enthalpy and entropy of formation of $SrCeO_3(s)$ at 1150 K derived from the data of Cordfunke et al. [9] are, respectively, $-1693.5 \pm 5.0\,kJ\,mol^{-1}$ and $-304 \pm 5.0\,J\,mol^{-1}\,K^{-1}$. It is seen that the enthalpy and entropy values derived from two different studies are in fairly good agreement considering the uncertainties involved in each case. The enthalpy and entropy of formation of $SrCeO_3(s)$ from the component oxides were derived at 1150 K from the calorimetric data [9] as $-5.4 \pm 10\,kJ\,mol^{-1}$ and $11.7 \pm 10\,J\,mol^{-1}\,K^{-1}$, respectively. From Galvanic measurement, Gopalan et al. [7] have reported theses thermodynamic quantities as $68.3\,kJ\,mol^{-1}$ and $106.812\,J\,mol^{-1}\,K^{-1}$, respectively. As against these reported results, the present study has derived these quantities from the decomposition pressure Eqs. (3) and (5) as $7.7 \pm 10\,kJ\,mol^{-1}$ and $7.5 \pm 10\,J\,mol^{-1}\,K^{-1}$, respectively. This study thus expresses $SrCeO_3(s)$ stability relative to its oxides as $\Delta G^0_{relative} = 7.7$ $(\pm 10) - 0.0075 \pm (0.010)T\,kJ\,mol^{-1}$. The present result as well as the reported ones [7,9] reveal an entropy increase during $SrCeO_3$ formation from its constituent oxides. The entropy and enthalpy values of Gopalan et al. are much higher than those derived from this study. In this regard the calorimetric results are quite in agreement with the present ones. However, this study derives a small endothermic value of the enthalpy.

The positive enthalpy value for $SrCeO_3$ could be predicted considering the reported correlation of the thermodynamic property with Goldschmidt tolerance factor (t) in perovskite formation [8]. According to the correlation, the relative enthalpy of formation for $A(II)M(IV)O_3$ type of perovskites is given by $\Delta H^0_{relative} = -120 + 1000(1-t)\,kJ\,mol^{-1},\ t = \{r(A) + r(O)\}/$ $[\sqrt{2}\{r(M) + r(O)\}];\ r(A),\ r(M),$ and $r(O)$ are Shannon's radii [17] for the A-site cations with 12 coordination, B-site cations with 6 coordination, and the oxide ions, respectively.

The calorimetrically derived results of negative enthalpy and positive entropy of formation of the cerate cannot explain the reported thermodynamic instability of the compound at lower temperatures ($\leqslant 639$ K) [7]. On the other hand, the positive values of enthalpy and entropy derived from this study do corroborate to the reported result that $SrCeO_3(s)$ is thermodynamically unstable with respect to the constituent oxides at low temperatures.

4. Conclusions

The results of tensimetric study of $CO_2(g)$ pressure over the triphasic mixture of $SrCO_3(s)$, $CeO_2(s)$ and $SrCeO_3(s)$ and over the biphasic mixture of $SrCO_3(s)$ and $SrO(s)$ corroborate well with the TG/DTA results

obtained at controlled pressures of CO_2 for the two systems. Thermodynamic properties of $SrCeO_3$ derived from the tensimetric studies suggest that the compound is thermodynamically unstable at lower temperatures. The derived properties are fairly in good agreement with that derived from calorimetry.

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