Available online at www.sciencedirect.com

SCIENCE DIRECT®

Thermochimica Acta 447 (2006) 101–105

thermochimica acta

www.elsevier.com/locate/tca

Thermodynamic stability of Sr_2CeO_4

A.N. Shirsat, K.N.G. Kaimal, S.R. Bharadwaj*, D. Das

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

Received 22 December 2005; received in revised form 29 March 2006; accepted 31 March 2006
Available online 15 April 2006

Abstract

Thermochemistry of the reaction between $SrCO_3$ and $SrCeO_3$, represented as

$$SrCO_3(s) + SrCeO_3(s) = Sr_2CeO_4(s) + CO_2(g),$$

was studied over the temperature range 1035–1135 K. The equilibrium pressure of $CO_2(g)$ over the ternary phase mixture of $SrCO_3(s)$, $SrCeO_3(s)$ and $Sr_2CeO_4(s)$ was measured at various temperatures by a tensimetric apparatus. The temperature dependence of the measured equilibrium $CO_2(g)$ pressure could be represented as

$$\ln \mathbf{p}_{CO_2}(\mathrm{Pa})(\pm 0.04) = \frac{-24742(\pm 550)}{T} + 28.43(\pm 0.55) \quad (1035 \le T(\mathrm{K}) \le 1115)$$

Simultaneous thermogravimetric (TG)/differential thermal analysis (DTA) experiments were carried out for reaction between $SrCO_3(s)$ and $CeO_2(s)$ in CO_2 atmosphere. The results were used to derive the thermodynamic properties of $Sr_2CeO_4(s)$.

Keywords: Strontium cerate; Sr_2CeO_4; Thermodynamic stability; Tensimetric studies; TG/DTA

1. Introduction

Ceria based solid solutions and compounds find applications in wide ranging areas, e.g. oxygen sensors, fuel cells, membrane reactors and inorganic pigments [1–5]. Some of the ternary oxides, such as $BaCeO_3$ and $SrCeO_3$ 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. These ternary oxides are also important in nuclear technology, as strontium, barium and cerium are important fission products, and it is known that a gray oxide phase (Ba,Sr) (U,Pu,Zr,RE,Mo)O_3 (RE = rare earth elements) with perovskite structure is formed in irradiated MOX (mixed oxide) fuel [9,10].

The compound Sr_2CeO_4 was recently discovered to exhibit blue luminescence [11]. Excitation with UV light, cathode rays and X-rays all produce luminescence in this material, and it has been established that undoped and doped Sr_2CeO_4 act as efficient blue-white and red phosphor materials [12]. The search for blue phosphors started more than 100 years ago and applications have regularly been developed, mainly in photonic and electro-luminescent devices. The luminescence of rare earth based phosphors also permits the development of trichromic luminescent lighting, the white colour being produced by the emission in the blue, green and red at 450, 550 and 610 nm, respectively. Satisfactory red and green commercial phosphors are being produced, but comparable materials in blue emission are still lacking [13,14] and are under development for practical applications [15,16]. Oxide based phosphors are most stable under electron excitation and there is a continuous search for new oxide phosphors that can give blue emission with high efficiencies and low accelerating voltages.

Sr_2CeO_4 has been synthesized and characterized by several workers [17–22]. During synthesis as well as in applications, it is important to know the compatibility of these materials with others. Chemical compatibility evaluation requires stability data on the oxides. In this context, the thermodynamic stability of $SrCeO_3$ was investigated by tensimetry [23]. The reported synthetic methods for undoped and doped Sr_2CeO_4 require high

---

* Corresponding author. Tel.: +91 22 2559 5100; fax: +91 22 2550 5151.
E-mail address: shyamala@apsara.barc.erent.in (S.R. Bharadwaj).

0040-6031/$ – see front matter © 2006 Published by Elsevier B.V.
doi:10.1016/j.tca.2006.03.026

temperature and hence thermodynamic stability of Sr_2CeO_4 is important. Although luminiscence and X-ray characterization of this compound is reported [17–22], its thermodynamic stability has not been studied so far. In this paper, we present equilibrium CO_2 pressure measurements for the reaction,

$$SrCeO_3 + SrCO_3 = Sr_2CeO_4 + CO_2(g) \tag{1}$$

determined by tensimetry and TG/DTA techniques and the thermodynamic properties derived from these studies.

2. Experimental

Sr_2CeO_4(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 900 °C for 4 h followed by heating at 1400 °C for 48 h in air with intermittent grinding. Thermogravimetric (TG) and differential thermal analysis (DTA) studies were carried out with a simultaneous TG-DTA apparatus (SETARAM 92-16.18), France) in flowing CO_2 gas, at a heating rate of 5 K/min. The recorded temperature scale of the TG profiles was precalibrated by the melting temperatures of pure silver and gold.

Powder XRD patterns of all the samples were recorded on a Philips X-ray Diffractometer (PW 1710) with Ni filtered Cu Kα radiation with silicon as an external standard.

For the tensimetric study, the compounds $SrCeO_3$ and Sr_2CeO_4 were freshly prepared and characterized by thermal and XRD analyses and stored in a vacuum desiccator. Typically, 500 mg powder sample was taken in a quartz reaction tube closed at one end and placed horizontally locating the sample in the isothermal zone of a resistance furnace equipped with controlled heating facility. The other end of the reaction tube was coupled to a manometer, made of pyrex glass, by a gas-tight joint. The manometer could measure pressure up to 7500 Pa with readability of 5 Pa. The system was coupled to high vacuum system through quick fit stopcock. The system could hold static vacuum over several weeks to better than the measuring sensitivity of 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 [24]. The temperature was measured to an accuracy of ±1 K.

After loading the sample in the tensimetric apparatus, the system was evacuated under a dynamic vacuum of 10^{-5} bar. Under evacuation, the sample temperature was raised to 773 K to release any absorbed moisture. The conditioning was continued until the static pressure of the system measured by the oil manometer became constant. The system was then isolated from the vacuum pump for taking the reading. The chemical path of reaction (1) was established by TG analysis and by recording the XRD patterns of the residual samples after the pressure measurements.

The equilibrium pressures of CO_2(g) for reaction (1) are the average of several readings taken at large time intervals as the system attained isothermal equilibrium, typically within half a day to a few days depending on the temperature. The room temperature fluctuated ±2 K, which corresponded to an insignificantly small uncertainty in the recorded height of the manometric fluid used in this study, viz., dibutyl phthalate oil (specific gravity 1.045 at 293 K).

3. Results and discussion

The XRD pattern for Sr_2CeO_4(s) was indexed based on a triclinic symmetry with $a = 0.6070$ nm, $b = 0.8976$ nm, $c = 1.0598$ nm, $\alpha = 94.8°$, $\beta = 90.4°$ and $\gamma = 95.8°$. The pattern matched with PCPDF file No. 22-1422 for Sr_2CeO_4 [25].

Thermogravimetric and differential thermal analysis curves for 2:1 mole mixture of $SrCO_3 + CeO_2$ in flowing CO_2 atmosphere can be seen in Fig. 1. The reactions corresponding to the three observed temperature effects in the TG/DTA curves can be summarized as follows:

$$\begin{gathered} SrCO_3(s)\quad \text{(orthorhombic)} = SrCO_3(s)\quad \text{(rhombohedral)} \\ \text{(phase transformation}\quad 1195\,\text{K)} \end{gathered} \tag{2}$$

$$SrCO_3(s) + CeO_2(s) = SrCeO_3(s) + CO_2(g) \quad (1441\,\text{K}) \tag{3}$$

and Eq. (1) $SrCeO_3(s) + SrCO_3(s) = Sr_2CeO_4(s) + CO_2(g)$ (1502 K).The observed phase transformation temperature of 1195 K is consistent with the reported value of 1197 K [26]. The observed mass losses (10.01 and 11.03 wt%) for reactions (3) and (1) agree with the proposed scheme of decomposition of 2:1 mixture of $SrCO_3$ and CeO_2 to form Sr_2CeO_4.

For tensimetric study of reaction (1), binary mixture of $SrCeO_3$(s) and $SrCO_3$(s), was used as the sample. As the system for reaction (1) was thermally cycled around a fixed temperature, fluid level in the manometer ultimately converged to a constant value. The gas pressure developed in the closed system, when changed temporarily, developed back to the same value at any fixed temperature. The attainment of pressure invariancy at

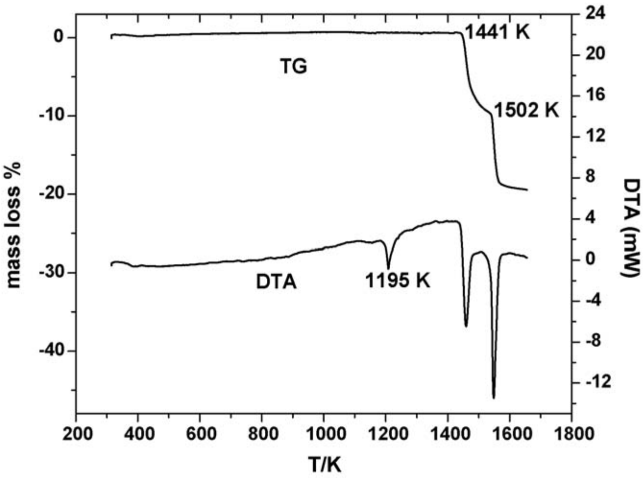

Fig. 1. TG-DTA curves for the reaction $2SrCO_3(s) + CeO_2(s) = Sr_2CeO_4(s) + 2CO_2(g)$ in one bar pressure of CO_2.
1195 K—phase transformation of $SrCO_3$(s)
1441 K—formation of $SrCeO_3$(s)
1502 K—formation of Sr_2CeO_4(s).

a temperature following thermal and mechanical perturbations was indicative of the reversibility and accomplishment of thermodynamic equilibrium.

The equilibrium vapour pressures of $CO_2(g)$ over the triphasic mixture of $SrCeO_3(s) + SrCO_3(s) + Sr_2CeO_4(s)$ at 1035–1115 K can be represented as,

$$\ln \mathbf{p}_{CO_2}(\mathrm{Pa})(\pm 0.04) = \frac{-24742(\pm 550)}{T} + 28.43(\pm 0.55) \quad (1035 \leq T(\mathrm{K}) \leq 1115) \tag{4}$$

with a co-relation co-efficient of $R = -0.998$.

To obtain a similar relation for this reaction for temperatures above the orthorhombic to rhombohedral phase transformation of $SrCO_3$, i.e., 1197 K, the magnitudes of the slope and intercept for the manometrically arrived vapour pressure Eq. (4) were corrected by the phase transformation enthalpy and entropy, respectively, 19,665 J mol^{-1} and 16.429 J K^{-1} mol^{-1} [26]. The small changes in enthalpy and entropy due to heat capacity changes over this temperature were neglected. The linear relation between ln $\mathbf{p}_{CO_2}$ and $1/T$ for reaction (1) for temperatures ≥1197 K is given by

$$\ln \mathbf{p}_{CO_2}(\mathrm{Pa})(\pm 0.04) = \frac{-22376(\pm 550)}{T} + 26.45(\pm 0.55) \quad (1197 \leq T(\mathrm{K})) \tag{5}$$

with a co-relation coefficient of $R = -0.998$.

From thermogravimetric result shown in Fig. 1, the decomposition temperature for reaction (1), observed in flowing CO_2 at 1 bar is 1502 ± 10 K. This observation is consistent with the calculated decomposition temperature of 1500 ± 10 K obtained from Eq. (5), which is valid for temperatures ≥1197 K. From Eq. (4), the mean enthalpy and entropy changes for reaction (1) could be determined as 205.7 ± 4.5 and 140.0 ± 4.0 J K^{-1} mol^{-1}, respectively.

To derive the Gibbs free energy of formation ($\Delta_f G^\circ$) of $Sr_2CeO_4(s)$ from the CO_2 partial pressures of reaction (1) expressed in Eq. (4), it is necessary to have the Gibbs free energy of formation ($\Delta_f G^\circ$) data of other compounds involved in the reaction. The Gibbs free energy of formation ($\Delta_f G^\circ$) of $Sr_2CeO_4(s)$ can be expressed as,

$$\Delta_f G^\circ(Sr_2CeO_4(s)) = \Delta_f G^\circ(SrCeO_3(s)) + \Delta_f G^\circ(SrCO_3(s)) - \Delta_f G^\circ(CO_2(g)) - RT\,\ln(\mathbf{p}_{CO_2}(\mathrm{bar})) \tag{6}$$

The available thermodynamic data on $SrCO_3(s)$ [26], was, however, found to be inconsistent with the decomposition temperature of $SrCO_3(s)$ observed at 1 bar pressure of CO_2 in the TG-DTA experiment [23,27]. The equilibrium $CO_2(g)$ pressures for the decomposition, calculated as a function of temperature, from the thermodynamic data for $SrCO_3(s)$, $SrO(s)$ and $CO_2(g)$ given in the compilation of Barin [26] indicate that the decomposition temperature of $SrCO_3(s)$ in 1 bar of $CO_2(g)$ to be 1426 ± 10 K. But the observed decomposition temperature from thermogravimetric results [23] is 1493 ± 15 K, as has been the observation of earlier workers as well [27]. In view of these TG results, the reported data of $\Delta_f G^\circ$ ($SrCO_3(s)$) [26] could not be used for deriving $\Delta_f G^\circ$ ($Sr_2CeO_4(s)$) from Eq. (6), instead the results from the tensimetric study in this laboratory [23] were used.

The Gibbs energy of $SrCe_2O_4(s)$ derived from the results of this study, i.e. from Eq. (4), and from the available thermodynamic data on $SrCeO_3(s)$ [23], $SrCO_3(s)$ [23] and $CO_2(g)$ [26] (data given in Table 1) is given by,

$$\Delta_f G^\circ(Sr_2CeO_4(s)) \ (\pm 7\,\mathrm{kJ\,mol^{-1}}) = -2285.9 + 0.42T \quad (1035 \leq T(\mathrm{K}) \leq 1115) \tag{7}$$

The Gibbs energy Eq. (7) was used to evaluate the stability of $Sr_2CeO_4(s)$ with respect to the decomposition reaction:

$$Sr_2CeO_4(s) = SrCeO_3(s) + SrO(s) \tag{8}$$

The Gibbs energy change for this reaction is given by

$$\Delta G^\circ_R = \Delta_f G^\circ(SrCeO_3(s)) + \Delta_f G^\circ(SrO(s)) - \Delta_f G^\circ(Sr_2CeO_4(s)) \tag{9}$$

For this, use was made of the reported data of $SrCeO_3(s)$ [23] and $SrO(s)$ [26] and Eq. (7). The free energy of the decomposition reaction (8) could be expressed as ΔG°_R (±10 kJ mol^{-1}) = $11.5 - 0.007T$. The obtained stability relation suggests that $Sr_2CeO_4(s)$ is unstable at higher temperatures. This corroborates the reported peritectoid decomposition of $Sr_2CeO_4(s)$ to $SrCeO_3(s)$ and $SrO(s)$ [28]. The decomposition temperature of 1643 K obtainable from the derived relation of ΔG°_R, is however, lower than the reported peritectoid of 1703 K [28]. The difference could be due to the uncertainty involved in the derived function of ΔG°_R.

The values of standard enthalpy and entropy of formation of $Sr_2CeO_4(s)$ obtained from (7) at the mean temperature of this study, i.e. 1075 K are −2286.9 ± 7 kJ mol^{-1} and −420 ± 7 J mol^{-1} K^{-1}, respectively. From this value of enthalpy of formation at high temperature, the standard enthalpy of formation at 298.15 K was calculated as −2272 ± 7 kJ mol^{-1}, from

Table 1
Thermodynamic data of $SrCeO_3(s)$ [23], $SrCO_3(s)$ [23], $SrO(s)$ [26] and $CO_2(g)$ [26]

Substances	Gibbs free energy equation
$SrCO_3(s)$	$\Delta_f G^\circ$ (±5 kJ mol^{-1}) = $-1206.0 + 0.25T$, $1045 \leq T(\mathrm{K}) \leq 1123$
$SrCeO_3(s)$	$\Delta_f G^\circ$ (±5 kJ mol^{-1}) = $-1680.5 + 0.31T$, $1113 \leq T(\mathrm{K}) \leq 1184$
$SrO(s)$	$\Delta_f G^\circ$ (±0.5 kJ mol^{-1}) = $-593.9 + 0.103T$, $1000 \leq T(\mathrm{K}) \leq 1200$
$CO_2(g)$	$\Delta_f G^\circ$ (±0.01 kJ mol^{-1}) = $-394.92 - 8.96 \times 10^{-4}T$, $1000 \leq T(\mathrm{K}) \leq 1500$

Table 2
Comparative analysis of thermodynamic data on Sr_2CeO_4(s) available in literature

$\Delta_f G^\circ$ (kJ/mol)	Temperature range (K)	$\Delta_f H^\circ_{298}$ (kJ/mol)	Method	Reference
$-2307 + 0.44T$ (±21)	805–1066	−2293.7[a] (±21)	E.M.F.	Pankajavalli et al. [30]
$-2285.9 + 0.42T$ (±7)	1035–1115	−2272.5[a] (±7)	Tensimetry	This work
		−2277.3 (±3.1)	Isoperibol calorimetry	Ali et al. [31]
		−2280.8	Estimation[b]	Yokokawa et al. [32]

[a] $\Delta_f H^\circ_{298}$ derived from the high temperature data of $\Delta_f G^\circ$.
[b] Estimation based on Goldschmidt's tolerance factor.

the relation,

$$\Delta_f H^\circ(1075\,\text{K}) = \Delta_f H^\circ(298.15\,\text{K}) + \int_{298.15}^{1075} \Delta\text{Cp}\,\text{d}T \qquad (10)$$

where

$$\Delta\text{Cp} = \text{Cp}(\text{Sr}_2\text{CeO}_4(\text{s})) - 2\text{Cp}(\text{Sr}(\text{s})) - \text{Cp}(\text{Ce}(\text{s})) - 2\text{Cp}(\text{O}_2(\text{g})) \qquad (11)$$

The required heat capacity for Sr_2CeO_4(s) was estimated by Kopp's rule [29], which states that the heat capacity of a double oxide can be obtained as a sum of heat capacities of the constituent oxides. Other heat capacity data are available from standard literature [26].

Pankajavalli et al. [30] have obtained Gibbs energy of formation of Sr_2CeO_4(s) by electro motive force (EMF) technique. The standard enthalpy and entropy of formation of Sr_2CeO_4(s) derived from their study at the mean temperature of their measurement, viz., 935 K are $-2307 \pm 20.0\,\text{kJ mol}^{-1}$ and $-440 \pm 20.0\,\text{J mol}^{-1}\,\text{K}^{-1}$, respectively. These values do not differ much from those reported in this work, but the decomposition temperature for reaction (8) derived from the EMF data [30] works out to be about 1000 K which is too low compared to the reported peritectoid temperature of 1703 K [28]. Ali et al. [31] have measured the standard enthalpy of formation of Sr_2CeO_4(s) by isoperibol calorimetry, and reported the value as $-2277.3 \pm 3.1\,\text{kJ mol}^{-1}$ at 298.15 K. Considering the uncertainty in the estimated thermal function of the compound, the derived value of $-2272 \pm 7\,\text{kJ mol}^{-1}$ for the enthalpy of formation in this investigation is in fairly good agreement with the calorimetric result.

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 $(A_2BO_4) = \Delta_f H^\circ$ (A_2BO_4)—$[2\Delta_f H^\circ$ $(AO) + \Delta_f H^\circ$ $(BO_2)]$, 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 [32]. 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 six 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 from the linear correlation equation. The enthalpy of formation of Sr_2CeO_4 derived from this stabilization energy works out to be $-2280.8\,\text{kJ mol}^{-1}$. This estimated value and all the other available thermodynamic data on Sr_2CeO_4 are compared in Table 2.

4. Conclusion

Gibbs free energy of formation of the technologically important compound Sr_2CeO_4 has been obtained by a simple tensimetric technique, backed by thermogravimetric results. The experimental thermodynamic data reported for Sr_2CeO_4, in this work is consistent with some of the stability data reported in literature. The Gibbs free energy of formation of Sr_2CeO_4 could be expressed as,

$$\Delta_f G^\circ(\text{Sr}_2\text{CeO}_4(\text{s}))(\pm 7\,\text{kJ mol}^{-1}) = -2285.9 + 0.42T \quad (1035 \le T(\text{K}) \le 1115)$$

From this equation, the standard molar enthalpy of formation of Sr_2CeO_4 could be derived as $\Delta_f H^\circ$ (298.15 K) $= -2272.5 \pm 7\,\text{kJ mol}^{-1}$. This value of the standard molar enthalpy of formation of Sr_2CeO_4 is consistent with the calorimetric result of $-2277.3 \pm 3.1\,\text{kJ mol}^{-1}$ and the estimated value of $-2280.8\,\text{kJ mol}^{-1}$.

References

[1] J. Fouletier, M. Henault, Solid State Ionics 9–10 (1983) 1277.
[2] T. Inoue, N. Seki, K. Eguchi, H. Arai, J. Electrochem. Soc. 137 (1990) 2523.
[3] S. Hamakawa, T. Hayakawa, A.P.E. York, T. Tsunoda, Y.S. Yoon, K. Suzuki, M. Shimizu, K. Takohira, J. Electrochem. Soc. 143 (1996) 1264.
[4] T. Mori, J. Drennan, Y. Wang, J.-G. Li, T. Ikegami, J. Therm. Anal. Calorim. (2002) 309.
[5] P. Sulcova, M. Trojan, J. Therm. Anal. Calorim. 65 (2001) 399.
[6] T. Takahashi, High Conductivity Solid Ionic Conductors, World Scientific, New Jersey, 1989, p. 166.
[7] N. Bonanso, Solid State Ionics 53 (1992) 967.
[8] H. Iwahara, Solid State Ionics 52 (1992) 99.
[9] H. Kleykamp, J. Nucl. Mater. 131 (1985) 221.
[10] H. Kleykamp, J.O. Pascoal, R. Pesja, F. Thommler, J. Nucl. Mater. 130 (1985) 426.
[11] E. Danielson, M. Devenney, D.M. Giaquinta, J.H. Golden, R.C. Haushalter, E.W. McFarland, D.M. Poojary, C.M. Reaves, W.H. Weinberg, X.D. Wu, Science 279 (1998) 837.
[12] R. Sankar, G.V. Subba Rao, J. Electrochem. Soc. 147 (2000) 2773.
[13] A.C. Vaz, de. Aranjo, L.T. Weber, B.S. Santos, B.J.P. Silva, R.P. Mello Jr., S. Alvies Jr., G.F. de Sa, C.M. Donoga, J. Non-Cryst. Solids 219 (1997) 160.
[14] C.R. Ronda, J. Alloys Compd. 225 (1995) 534.
[15] M. Dejneka, E. Smitzev, R.E. Riman, J. Lumin. 65 (1995) 227.

[16] H. Yamamoto, M. Mikarni, Y. Shimomura, Y. Oguni, J. Lumin. 87 (2000) 1079.

[17] S.J. Chen, X.T. Chen, Zhi Yu, J.M. Hong, Z. Xue, X.Z. You, Solid State Commun. 130 (2004) 281.

[18] X. Yu, X.H. He, S.P. yang, X. Yang, X. Xu, Mater. Lett. 58 (2004) 48.

[19] Y.B. Khollam, S.B. Deshpande, P.K. Khanna, P.A. Joy, H.S. Potdar, Mater. Lett. 58 (2004) 2521.

[20] T. Masui, T. Chiga, N. Imanaka, G. Ada Chi, Mater. Res. Bull. 38 (2003) 17.

[21] O.A. Serra, V.P. Severino, P.S. Calefi, S.A. Ciciuini, J. Alloys Compd. 232–234 (2001) 667.

[22] E. Danielson, M. Devenney, D.M. Oiaquinta, J.H. Golden, R.C. Haushalter, E.W. Mc Farland, D.M. Ppjary, C.M. Reaves, W.H. Weinberg, X.D. Wu, J. Mol. Struct. 470 (1998) 229.

[23] A.N. Shirsat, K.N.G. Kaimal, S.R. Bharadwaj, D. Das, J. Solid State Chem. 177 (2004) 2007.

[24] International Practical Temperature Scale, Metrologia 5 (1969) 35.

[25] PCPDFWIN version 1.30, JCPDS—International Centre for Diffraction Data, PDF-2 Data Base (Sets 1-47), Copyright ©JCPDS—ICDD, 1997.

[26] I. Barin, Thermochemical Data of Pure Substances, third ed., VCH, Weinheim, 1995.

[27] M.J. Scholten, J. Schoonman, J.C. van Miltenburg, H.A.J. Oonk, in: S.C. Singhal, H. Iwahara (Eds.), Proceedings of Third International Symposium on Solid Oxide Fuel Cells , vol. 93–4, Electrochemical Society, 1993, pp. 146–155.

[28] V. Longo, D. Minichelli, F. Ricciardiello, Sci. Ceram. 11 (1981) 171.

[29] O. Kubaschewski, C.B. Alcock, Metallurgical Thermochemistry, fifth ed., Pergamon, New York, 1979.

[30] R. Pankajavalli, K. Ananthasivan, S. Anthonysamy, P.R. Vasudeva Rao, J. Nucl. Mater. 336 (2005) 177.

[31] M. Ali (Basu), R.V. Wandekar, S.R. Bharadwaj, D. Das, J. Thermal Anal. Calorim. 78 (2004) 715.

[32] H. Yokokawa, N. Sakai, T. Kawada, M. Dokiya, J. Solid State Chem. 94 (1991) 106.