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Enthalpies of Formation of $La_{1-x}A_xMnO_{3\pm\delta}$ (A = Ca and Sr) Measured by High-Temperature Solution Calorimetry

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High-temperature reaction calorimetry using molten lead borate as a solvent has been used to study the thermochemistry of $La_{1-x}A_xMnO_3$ (A = Ca and Sr, $0 \leq x \leq 1$). The structural properties and the oxygen stoichiometry of the calcined powders were characterized by powder X-ray diffraction, thermogravimetry, and iodometry. The enthalpy of formation of the materials from their binary constituents has been calculated from measured enthalpy of solutions. The enthalpy of formation of $La_{1-x}Ca_xMnO_3$ from the component oxides becomes more exothermic with increasing substitution level x due to the increasing valence state of Mn, and demonstrates a nearly linear dependence of the average valence state of manganese. $La_{1-x}Sr_xMnO_3$ has a significantly more exothermic enthalpy of formation from the binary constituents than the Ca-substituted materials, and demonstrates a negative deviation from ideal behavior. The present thermodynamic data are discussed in relation to the Goldschmidt tolerance factor for the perovskite structure. Finally, the phase stability of Sr- and Ca-substituted $LaMnO_3$ is addressed in relation to the application of these materials in solid oxide fuel cells. © 2002 Elsevier Science

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INTRODUCTION

Calcium- and strontium-substituted lanthanum manganites, $La_{1-x}A_xMnO_3$ (A = Sr or Ca), are of technological importance for use as cathodes in solid oxide fuel cells (SOFCs) (1–3). These materials have high electronic conductivity and high ionic conductivity at high substitution levels (4–6). Recently, $La_{1-x}A_xMnO_3$ materials have also received considerable attention due to their magnetoresistance (7, 8). Despite the considerable interest in these materials, the thermodynamic properties of the solid solutions have not been thoroughly investigated. Thermodynamic properties are essential in order to understand their behavior in SOFCs. In particular, their chemical stability and their reactivity with other materials in SOFCs can only be described thoroughly on the basis of a thermodynamic analysis.

So far only a limited number of thermodynamic investigations of Mn-based perovskites have been reported. Laberty *et al.* (9) have measured, by high-temperature drop solution calorimetry, the enthalpy of formation of $NdMnO_3$, $YMnO_3$, $La_{1-x}Sr_xMnO_3$ (with $0 \leq x \leq 0.5$), and $Ln_{0.5}Ca_{0.5}MnO_3$ (with Ln = La, Nd, Y). They discussed the thermodynamic data in terms of the size of the A-site cation (A = La, Nd, Y), the valence of Mn, and the Goldschmidt tolerance factor. A considerable amount of work has been performed to determine the thermodynamic properties of $LaMnO_{3\pm\delta}$. Most of the thermodynamic data have been obtained by thermogravimetric analyses of the decomposition of $LaMnO_{3\pm\delta}$ to the binary constituents (10–16). Atsumi *et al.* (10) have compared and evaluated these data. Yokokawa *et al.* (17–19) have also offered a review on the thermodynamic properties of perovskite materials, but most of these data are estimated.

We have started a program to investigate the thermodynamic properties of the solid solutions $La_{1-x}A_xMnO_{3\pm\delta}$ (A = Ca or Sr, $0 \leq x \leq 1$). Here, we report on the enthalpy of formation of $La_{1-x}A_xMnO_{3\pm\delta}$ from the binary oxides found by high-temperature solution calorimetry. In addition measurements of the enthalpy of oxidation of $CaMnO_{3-\delta}$, $Ca_2MnO_{4-\delta}$, and $SrMnO_{3-\delta}$ by *in situ* adiabatic calorimetry (20), the heat capacity of $CaMnO_{2.562}$ and $SrMnO_{2.598}$ by adiabatic calorimetry (21), and finally studies of phase diagrams and oxygen nonstoichiometry (22) are reported in separate papers. The phase diagram studies (22) have revealed that the $La_{1-x}Ca_xMnO_{3\pm\delta}$ solid solutions are stable solutions, while the solid solubility of α-$SrMnO_3$ in $LaMnO_{3\pm\delta}$ is limited below the α-β $SrMnO_3$ phase transitions. $La_{1-x}Sr_xMnO_{3\pm\delta}$ ($x > 0.2$) studied here is therefore metastable with respect to α-$SrMnO_3$ and $La_{1-x}Sr_xMnO_{3+\delta}$ ($x \sim 0.2$–0.3).

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EXPERIMENTAL PROCEDURE

Synthesis

Calcium (LCM)- and strontium (LSM)-substituted lanthanum manganite with 0, 20, 40, 60, 80, and 100 mol% substitution were synthesized by the amorphous citrate process or the EDTA precursor method. The preparation of the samples is described elsewhere (22). The powders were calcined in air at 1000–1400°C for 24–200 h in order to obtain phase pure materials. The higher temperatures were used for the materials with high Sr substitution to avoid the precipitation of α-$SrMnO_3$. $LaMnO_{3.045}$ was prepared by heat treatment of $LaMnO_{3+\delta}$ in nitrogen for 200 h at 900°C.

Metastable perovskite $SrMnO_{3-\delta}$ was obtained by quenching cylindrical disks of $SrMnO_{3.0}$ annealed at 1525°C in air for 2 h. This gave a cylindrical body where the outer surface was hexagonal α-$SrMnO_{3-\delta}$ (due to oxidation during cooling), while the interior of the cylinder was pure perovskite β-$SrMnO_{3-\delta}$. These two phases were easily separated due to color differences, and all further handling and measurements were performed on the metastable perovskite phase of $SrMnO_3$. The crystal structure of the perovskite $SrMnO_{3-\delta}$ was confirmed by X-ray diffraction.

Characterization of Materials

Lattice cell dimensions of the materials was determined by X-ray diffraction (SIEMENS D5005, Siemens Germany) using CuKα radiation. Silicon was used as an internal standard. The oxygen stoichiometry of the samples was determined by thermogravimetric analyses and iodometric titration described previously (22).

Calorimetry

High-temperature solution calorimetry was performed on a single Calvet-type reaction calorimeter. The single thermopile is similar to the ones used in a twin Calvet-type calorimeter previously described by Navrotsky (23). Three Kanthal heating elements were used to keep a stable temperature across the thermopile. An Al_2O_3 heat reservoir was placed between the heating elements and the thermopile. This calorimeter measures heat flow through the sensitive thermopile; the signal is recorded as a curve of voltage versus time, the area under which is proportional to the heat effect. Details regarding construction of the single Calvet-type calorimeter are given elsewhere (24).

We have used a similar experimental set-up for the measurement of heat of solution as described by Navrotsky (25, 26) with some changes given here. The set-up is mounted in a fused silica liner, which is easy to remove from the calorimeter for sample preparations. Inside the liner is a protective Pt crucible, which contains a Pt crucible with the lead borate solvent. The sample, which is going to be dissolved in the solvent, is contained in a small Pt basket located above the solvent. The wall of the basket is made of a Pt net, which makes the dissolution of the sample easier since the solvent can circulate through the Pt net. The sample basket is attached to a mullite tube, which extends above the top of the calorimeter. A stirrer is located inside this tube, where the lower part is made of platinum and the upper part is an alumina rod. The mullite tube and the alumina rod can be moved independently from the outside of the calorimeter. Vertical heat loss through the silica liner is limited by horizontal radiation shields.

The calorimeter was calibrated by dropping Pt rods of known mass and heat content into the Pt crucible. This was done frequently, and no changes in the calibration constant were observed either over time or when the silica liner was changed. The standard deviation in the calibration constant is $\pm 5.7\%$.

The solution experiments were performed in a gas flow of synthetic air or nitrogen depending on the sample. The experiments (4–9 experiments per sample) were performed at 993 K, and molten lead borate ($2PbO \cdot B_2O_3$) was used as a solvent for all materials (solvent replaced every third experiment). Powder samples of 40–100 mg contained in the sample Pt container were kept right above the solvent until thermal equilibrium was reached. At thermal equilibrium the recording of the thermopile voltage was started. The Pt basket containing the sample was then lowered into the solvent by using the mullite tube extending out of the calorimeter. The sample was stirred into the solvent using the alumina rod attached to the stirrer. This was done 3–4 times in a row in a short time. After the reaction was completed and the calorimetric signal had returned to the steady state value, a second stirring run was performed. The "stirring effect" was determined 3–4 times. Deviations between the "stirring effects" indicated problems with the experiment. The heat contribution from stirring only was subtracted from the experimental enthalpy of reaction to allow the measurement of the enthalpy of solution. The heat effect of the stirring varied between 3–80% of the measured enthalpy of solution of the studied materials. The enthalpy due to stirring was reproducible and relatively constant, but the contribution to the measured enthalpy changed as the enthalpy of solution and the amount of material dissolved varied. The heat due to the solution of the sample and the stirring effects were obtained by integrating the thermopile voltage versus time. The steady stage voltage was used as the baseline in the integration. After each experiment, the lead borate was examined by optical microscopy to ensure that the entire sample had been dissolved during the experiment.

TABLE 1
Unit Cell Parameters and Oxygen Stoichiometry for $La_{1-x}A_xMnO_{3\pm\delta}$ (A = Ca or Sr, $0 \leq x \leq 1$)[a]

X	$3 \pm \delta$ at 993 K	a (Å)	b (Å)	c (Å)
0.0	3.148	5.5248(4)	—	13.331(1)
0.0	3.045 (in N_2)	5.6905(7)	7.712(1)	5.538(1)
Ca = 0.2	3.065	5.497(3)	7.740(4)	5.473(4)
Ca = 0.4	3.001	5.456(2)	7.685(2)	5.445(1)
Ca = 0.6	3.000	5.402(2)	7.599(3)	5.398(3)
Ca = 0.8	3.000	5.335(3)	7.549(4)	5.332(3)
Ca = 1.0	2.996	5.277(2)	7.467(5)	5.274(3)
Sr = 0.2	3.051	5.5155(2)	—	13.3543(7)
Sr = 0.4	3.000	5.487(1)	—	13.35(1)
Sr = 0.6	3.000	7.681(1)	—	7.736(2)
Sr = 0.8	3.000	3.8281(1)	—	—
Sr = 1.0	2.946	3.8061(1)	—	—

[a] $LaMnO_{3.045}$, $La_{0.8}Ca_{0.2}MnO_{3.065}$, $La_{0.6}Ca_{0.4}MnO_{3.001}$, $La_{0.4}Ca_{0.6}MnO_{3.000}$, $La_{0.2}Ca_{0.8}MnO_{3.000}$, and $CaMnO_{2.996}$ were found to be orthorhombic. $LaMnO_{3.148}$, $La_{0.8}Sr_{0.2}MnO_{3.051}$, and $La_{0.6}Sr_{0.4}MnO_{3.000}$ were rhombohedral, $La_{0.4}Sr_{0.6}MnO_{3.000}$ was tetragonal, and $La_{0.2}Sr_{0.8}MnO_3$ and $SrMnO_{2.946}$ had cubic crystal structure.

RESULTS

The oxygen stoichiometry at 993 K (720°C) and the lattice parameters at room temperature for the $La_{1-x}A_xMnO_{3\pm\delta}$ (A = Sr or Ca) compounds with $0 \leq x \leq 1$ are given in Table 1. The X-ray diffraction data demonstrated that all samples were single phase except $CaMnO_3$. The effect of the minor amounts of a secondary phase, $CaMn_2O_4$, in $CaMnO_3$ was neglected in the following. The oxygen defect chemistry and crystal structure of the materials are further described in a separate paper (22).

The enthalpies of solution of CaO, La_2O_3, and Mn_2O_3 were measured in separate experiments. The data are given in Table 2. We measured the enthalpy of solution of $SrCO_3$ instead of the corresponding data for SrO due to problems with the hygroscopic nature of SrO (25). The enthalpy of solution of SrO was determined from the enthalpy of solution of $SrCO_3$ by using a thermodynamic cycle:

$$\Delta H_1 \; SrCO_3\ (s, 993\ K) \rightarrow SrO\ (sol, 993\ K) + CO_2\ (g, 993\ K) \qquad [1]$$

$$\Delta H_2 \; SrO\ (s, 993\ K) + CO_2\ (g, 993\ K) \rightarrow SrCO_3\ (s, 993\ K) \qquad [2]$$

$$\Delta H_3 \; SrO\ (s, 993\ K) \rightarrow SrO\ (sol, 993\ K). \qquad [3]$$

In this equation $\Delta H_3 = \Delta H_1 + \Delta H_2$. ΔH_1 is the measured enthalpy of solution of $SrCO_3$, while ΔH_2 is the enthalpy of formation of $SrCO_3$ from SrO and CO_2 calculated from tabulated values (27). The calculated enthalpy of solution of SrO is given in Table 2.

The enthalpy of solution of the materials $La_{1-x}A_xMnO_{3\pm\delta}$ (A = Ca or Sr) is given in Table 2. The enthalpy of solution is represented by the reaction (at 993 K):

$$La_{1-x}A_xMnO_{3\pm\delta}\ (s) = (1-x)/2\ La_2O_3\ (sol) + xAO\ (sol) + \tfrac{1}{2}Mn_2O_3\ (sol) + (x \mp \delta)/4\ O_2\ (g). \qquad [4]$$

The enthalpy of formation of the $La_{1-x}A_xMnO_{3\pm\delta}$ series from the component oxides have been calculated from the measured enthalpy of solutions using a thermodynamic cycle:

$$-\Delta H_5 \quad La_{1-x}A_xMnO_3\ (s, 993\ K) \rightarrow (1-x)/2La_2O_3\ (sol, 993\ K) + xAO\ (sol, 993\ K) + \tfrac{1}{2}Mn_2O_3\ (sol, 993\ K) + x/4O_2\ (g, 993\ K) \qquad [5]$$

$$\Delta H_6 \quad (1-x)/2La_2O_3\ (s, 993\ K) \rightarrow (1-x)/2La_2O_3\ (sol, 993\ K) \qquad [6]$$

$$\Delta H_7 \quad xAO\ (s, 993\ K) \rightarrow xAO\ (sol, 993\ K) \qquad [7]$$

$$\Delta H_8 \quad \tfrac{1}{2}Mn_2O_3\ (s, 993\ K) \rightarrow \tfrac{1}{2}Mn_2O_3\ (sol, 993\ K) \qquad [8]$$

$$\Delta H_9 \quad (1-x)/2\ La_2O_3\ (s, 993\ K) + xAO\ (s, 993\ K) + \tfrac{1}{2}Mn_2O_3\ (s, 993\ K) + x/4\ O_2\ (g) \rightarrow La_{1-x}A_xMnO_3\ (s, 993\ K). \qquad [9]$$

TABLE 2
Enthalpy of Solution (ΔH_{sol}) and Enthalpy of Formation from the Binary Oxides (ΔH_9) and the elements ($\Delta_f H^\circ$) at 993 K (720°C) for $La_{1-x}A_xMnO_{3\pm\delta}$ (A = Ca or Sr)[a]

Compound	ΔH_{sol} (kJ/mol)	ΔH_9 (kJ/mol)	$\Delta_f H^\circ$ [kJ/mol]
La_2O_3	-125.1 ± 6.3 (5)	—	—
Mn_2O_3	64.9 ± 8.4 (6)	—	—
CaO	-58.1 ± 5.3 (6)	—	—
$SrCO_3$	133.2 ± 8.4 (7)	—	—
SrO	-95.3 ± 8.4[b]	—	—
$LaMnO_{3.148}$	35.5 ± 3.9 (5)	-65.6 ± 6.2	-1435.4
$LaMnO_{3.045}$	25.9 ± 6.4 (6)	-56.1 ± 8.2	-1425.9
$La_{0.8}Ca_{0.2}MnO_{3.065}$	55.2 ± 4.0 (8)	-84.4 ± 6.2	-1401.7
$La_{0.6}Ca_{0.4}MnO_{3.001}$	61.3 ± 6.7 (7)	-89.6 ± 8.2	-1356.5
$La_{0.4}Ca_{0.6}MnO_{3.000}$	71.4 ± 5.8 (5)	-98.8 ± 7.5	-1314.4
$La_{0.2}Ca_{0.8}MnO_{3.000}$	93.1 ± 7.3 (8)	-119.6 ± 8.8	-1283.6
$CaMnO_{2.996}$	99.7 ± 5.4 (9)	-125.4 ± 7.6	-1238.0
$La_{0.8}Sr_{0.2}MnO_{3.051}$	74.8 ± 7.4 (5)	-111.5 ± 8.8	-1421.3
$La_{0.6}Sr_{0.4}MnO_{3.000}$	79.3 ± 3.6 (6)	-122.5 ± 6.0	-1372.3
$La_{0.4}Sr_{0.6}MnO_{3.000}$	89.0 ± 4.5 (6)	-138.8 ± 6.7	-1328.5
$La_{0.2}Sr_{0.8}MnO_{3.000}$	99.6 ± 6.8 (5)	-155.9 ± 8.7	-1285.6
$SrMnO_{2.946}$	68.6 ± 2.4 (7)	-131.5 ± 6.4	-1201.2

[a] The figures in brackets are the number of experiments used to calculate the standard deviation.

[b] Calculated from the heat of solution of $SrCO_3$.

In this equation $\Delta H_9 = -\Delta H_5 + \Delta H_6 + \Delta H_7 + \Delta H_8$. The enthalpy of solution at 993 K for $La_{1-x}A_xMnO_3$, La_2O_3, AO, and Mn_2O_3 are ΔH_5, ΔH_6, ΔH_7, and ΔH_8, respectively. Table 2 summarizes the enthalpy for the formation reaction [9] for the different materials.

DISCUSSION

Materials

The unit cell dimensions given in Table 1 are all in good agreement with the literature (1,28–35). A more thorough discussion of the crystal structure versus composition is given elsewhere (22). The oxygen nonstoichiometry for each sample given in Table 1 demonstrates that *LAM* (A = Sr or Ca) with $x = 0.0$ and 0.2 are oxygen excess materials, while $CaMnO_3$ and $SrMnO_3$ are oxygen deficient at 993 K.

Enthalpy of Formation from Binary Oxides

The enthalpy of solution of the binary oxides at 993 K given in Table 2 is in good accord with literature data measured at 976 or 977 K (-58.9 ± 1.4, 135.4 ± 1.0, -126.0 ± 4.4, and 63.8 ± 1.6 kJ/mol for CaO, $SrCO_3$, La_2O_3, and Mn_2O_3, respectively) (25,36,37). This confirms that the thermodynamic data obtained by the present calorimeter are in accord with previous high temperature calorimetric investigations. However, our typical standard deviation is approximately 8%, which is higher than obtained in Navrotsky's laboratory (23). The higher uncertainty is caused by the significant stirring effect in the present study.

Enthalpies of formation of both $LaMnO_{3.148}$ and $LaMnO_{3.045}$ from the component oxides have been measured, Table 2. A higher oxygen stoichiometry gives a more exothermic enthalpy of formation. These values were used to estimate an enthalpy of oxidation for the hypothetical reaction

$$LaMnO_3 + \tfrac{1}{4}O_2(g) = LaMnO_{3.5}, \qquad [10]$$

giving -184.5 kJ/mol O_2. This is far less exothermic than -340.5 and -293.0 kJ/mol O_2 previously found for $CaMnO_{3-\delta}$ and $SrMnO_{3-\delta}$, respectively (20). However, this is indeed expected as reaction [10] also involves the formation of cation vacancies ($LaMnO_{3+\delta}$ can alternatively be described as $La_{3/(3+\delta)}Mn_{3/(3+\delta)}O_3$ to point out the presence of cation vacancies). In addition La_2O_3 is also more acidic than CaO and SrO, and a lower stability of Mn(IV) in $LaMnO_{3+\delta}$ relative to $CaMnO_3$/$SrMnO_3$ is expected.

From the enthalpy of oxidation of lanthanum manganite, Eq. [10], the enthalpy of formation from the binary oxides of the stoichiometric phase ($LaMnO_{3.00}$) is found to be -51.9 ± 8.2 kJ/mol at 993 K. Thermodynamic data for the binary oxides were taken from Barin (27). The enthalpy is in good accord with the data obtained by decomposition measurements by Atsumi *et al.* (10) (-51.7 kJ/mol at 1000 K).

The enthalpy of formation from the binary oxides (Eq. [9] with $x = 1$ and $\delta = 0$) for $SrMnO_{3.00}$ is found to be -139.4 ± 6.4 kJ/mol using the enthalpy of oxidation of $SrMnO_{3-\delta}$ reported by Rørmark *et al.* [20] (-293.0 kJ/mol). The enthalpy of formation from the binary oxides of the slightly oxygen-deficient $CaMnO_{2.996}$ is not corrected, due to a larger influence given by the standard deviation of the enthalpy of solution (Table 2). As no enthalpy of oxidation is known for LSM and LCM with $x = 0.2$, a linear relationship of the enthalpy of oxidation of the end members as a function of substitution is assumed. The enthalpies of formation from the binary oxides of the two stoichiometric compounds with 20 mol% of substitution were then calculated to be $\Delta H_9(La_{0.8}Ca_{0.2}MnO_{3.00}) = -77.4 \pm 6.2$ kJ/mol and $\Delta H_9(La_{0.8}Sr_{0.2}MnO_{3.00}) = -106.2 \pm 8.8$ kJ/mol.

From the enthalpies of oxidation of $CaMnO_{3-\delta}$ and $SrMnO_{3-\delta}$ (20) and the enthalpy of formation of the stoichiometric perovskites, the enthalpies of formation of 0.5 mole of $Sr_2Mn_2O_5$ and $Ca_2Mn_2O_5$ from the binary oxides were estimated to be -66.2 ± 6.4 and -40.5 ± 7.6 kJ/mol, respectively. The estimated enthalpy of formation of $Sr_2Mn_2O_5$ is in good accord with -62.7 kJ/mol (at 1173 K) found by the solid oxide electrolyte galvanic cell method (38).

The enthalpy of formation from the binary oxides of stoichiometric $La_{1-x}Sr_xMnO_3$ and $La_{1-x}Ca_xMnO_3$ is given in Fig. 1 as a function of degree of substitution. It is

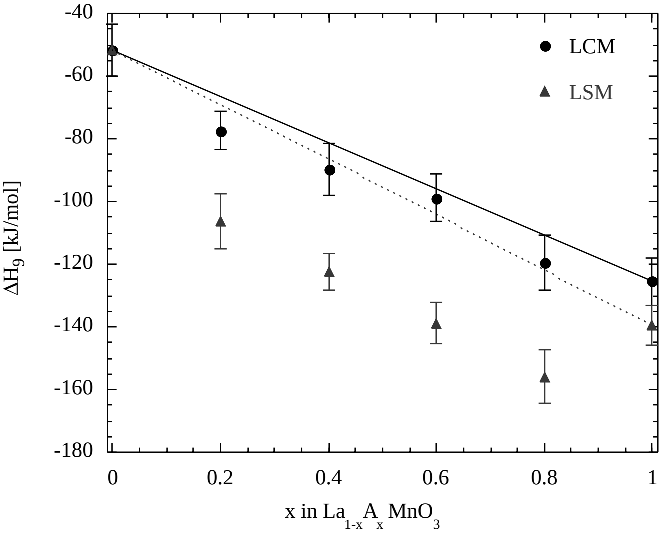

FIG. 1. Enthalpy of formation from binary oxides of stoichiometric $La_{1-x}Ca_xMnO_3$ (solid circles) and $La_{1-x}Sr_xMnO_3$ (solid up triangles) from the binary oxides as a function of the degree of substitution. The solid and the dotted lines represent ideal solid solutions of LCM and LSM, respectively. The error bars are the standard deviation of 5–9 measurements of the enthalpy of solution of the actual sample.

shown that the enthalpy of formation of both LSM and LCM decreases with increasing x, except for the metastable $SrMnO_3$ (which transforms to a hexagonal phase at 1073 K) (32). This is in good accord with the assumption that the enthalpy of formation from the binary oxides becomes more exothermic with an increasing amount of Mn^{4+}. The enthalpy of formation of LSM is significantly more exothermic than for LCM, which is expected since SrO is more basic than CaO. This trend is also found for ATiO$_3$ and AZrO$_3$ (A = Sr and Ca) systems (39).

Ideal solid solution of LCM and LSM,

$$\Delta_{\mathrm{mix}}H(\mathrm{La}_{1-x}A_x\mathrm{MnO}_3) = x\cdot\Delta H_9(A\mathrm{MnO}_3) + (1-x)\cdot\Delta H_9(\mathrm{LaMnO}_3), \quad [11]$$

is given by the solid and dotted lines in Fig. 1, respectively. The $La_{1-x}Ca_xMnO_3$ system shows a nearly ideal solid solution behavior. The unit cell volume of LCM has been found to decrease linearly with increasing amount of Ca (22) and shows good agreement with the nearly ideal behavior found by calorimetry. The $La_{1-x}Sr_xMnO_3$ system shows a negative deviation from ideal behavior. The unit cell volume versus composition is however nearly linear as in the LCM system (22).

The enthalpy of formation from the binary oxides of $La_{0.5}Ca_{0.5}MnO_3$ and LSM with $x = 0.1$, 0.3, and 0.5 found by Laberty *et al.* (9) is significantly less exothermic than the present data. The reported unit cell parameters for $LaMnO_3$ are not in good accord with literature. According to the data reported by Laberty *et al.* (9), the enthalpies of formation from the binary oxides of $La_{1-x}A_xMnO_3$ (A = Ca, Sr) show no apparent trend with the A content. We would however expect the enthalpy of formation to become more exothermic with increasing A content (increasing content of Mn^{4+}) as shown in Fig. 1 due to the high enthalpy of oxidation of $CaMnO_{3-\delta}$ and $SrMnO_{3-\delta}$ (20). Finally, the data reported by Laberty *et al.* (9) have not been corrected for the oxygen nonstoichiometry of the samples, but taking this into account does not result in a better agreement with the present data.

Relationship between Crystal Structure and Enthalpy of Formation

The distortion of the perovskite lattice is given by the Goldschmidt tolerance factor:

$$t = (r_{\mathrm{A}} + r_{\mathrm{O}})/(\sqrt{2}(r_A + r_O)), \quad [12]$$

where r_{A}, r_{B}, and r_{O} are the ionic radii of the A and B cations and the oxygen anion, respectively. Figure 2 shows the enthalpy of formation of stoichiometric LCM and LSM, from the binary oxides, as a function of the Goldschmidt tolerance factor. The tolerance factor for ABO$_3$ was calculated with coordination numbers (CN) 12, 6, and 6 for A, B, and O ions, respectively. For $A_2B_2O_5$ CNs of 10, 5, and 6 were used. The ionic radii were taken from Shannon (40). The enthalpy of formation from the binary oxides is found to increase with decreasing $1 - t$ (see Fig. 2), which has been shown previously by Yokokawa *et al.* (41).

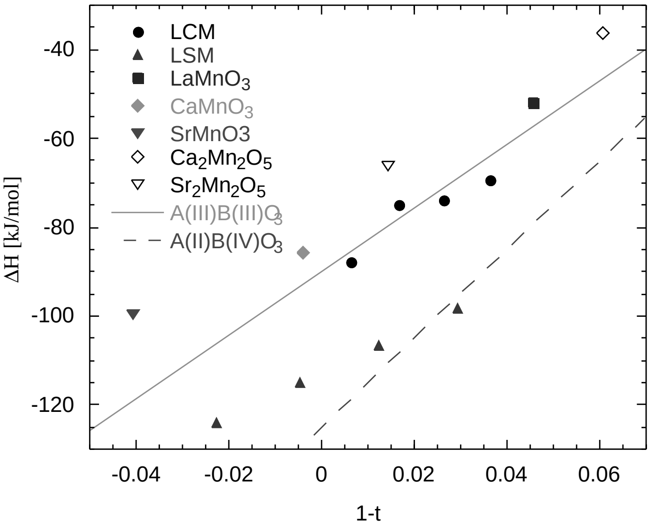

FIG. 2. Enthalpy of formation from binary oxides of stoichiometric $La_{1-x}Ca_xMnO_3$ and $La_{1-x}Sr_xMnO_3$ as a function of the Goldschmidt tolerance factor. Solid symbols are for stoichiometric perovskites while open symbols are $Ca_2Mn_2O_5$ and $Sr_2Mn_2O_5$. The solid and broken lines are the relations found for the perovskites $A^{\mathrm{III}}B^{\mathrm{III}}O_3$ and $A^{\mathrm{II}}B^{\mathrm{IV}}O_3$, respectively (41).

Phase Stability

Two different reaction paths may occur when the present materials are exposed to high temperatures or low partial pressure of oxygen. First, $La_{1-x}Ca_xMnO_3$ and $La_{1-x}Sr_xMnO_3$ will lose oxygen and become oxygen deficient:

$$\mathrm{La}_{1-x}A_x\mathrm{MnO}_3 = \mathrm{La}_{1-x}A_x\mathrm{MnO}_{3-\delta} + \tfrac{\delta}{2}\mathrm{O}_2(\mathrm{g}). \quad [13]$$

Second, they may decompose at sufficiently low partial pressure of O_2:

$$\mathrm{La}_{1-x}A_x\mathrm{MnO}_{3-\delta} = \mathrm{MnO} + \frac{1-x}{2}\mathrm{La}_2\mathrm{O}_3 + xA\mathrm{O} + \frac{1-2\delta+x}{4}\mathrm{O}_2(\mathrm{g}). \quad [14]$$

The enthalpies of oxidation of $LaMnO_{3+\delta}$, $CaMnO_{3-\delta}$, and $SrMnO_{3-\delta}$ presented in the previous discussion correspond to the oxidation of Mn^{3+} to Mn^{4+}. Using a linear relationship for the enthalpy of oxidation of the end members and the enthalpy of formation of the stoichiometric $La_{1-x}A_xMnO_{3.0}$ (A = Ca or Sr), the enthalpy of formation of $La_{1-x}A_xMnO_{3-\delta}$ containing only Mn^{3+} can be

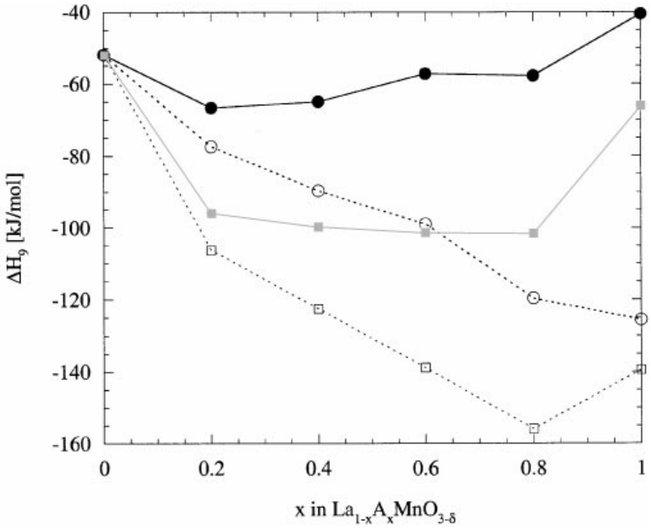

FIG. 3. Enthalpy of formation from the binary oxides of $La_{1-x}Ca_xMnO_3$ (circles) and $La_{1-x}Sr_xMnO_3$ (squares) as a function of Ca and Sr substitution. Open symbols represent stoichiometric materials, while filled symbols represent the estimated enthalpy of formation of the hypothetical materials $La_{1-x}A_xMnO_{3-x/2}$ containing only Mn^{3+}.

calculated. The estimations are shown in Fig. 3 together with the enthalpy of formation of the stoichiometric compounds. The estimated enthalpies of formation from the binary oxides of LCM and LSM containing only Mn^{3+} are exothermic, and it is expected that it should be possible to obtain the oxides as stable or metastable phases in line with experimental findings (22, 42).

A further reduction of the oxygen content reduces Mn^{3+} to Mn^{2+}. The enthalpy involved in the reduction of Mn^{3+} to Mn^{2+} is expected to be significantly higher than the enthalpy of reduction of Mn^{4+} to Mn^{3+} (20). The enthalpy of oxidation of Mn^{2+} to Mn^{3+} can be estimated on the basis of a comparison with the corresponding data for the enthalpies of formation of MnO, Mn_2O_3 and MnO_2 (37). The enthalpies of the following reactions at 977 K are − 158.4 and − 352.8 kJ/mol O_2, respectively:

$$2Mn_2O_3 + O_2 = 4MnO_2 \qquad [15]$$

$$4MnO + O_2 = 2Mn_2O_3. \qquad [16]$$

The enthalpy of oxidation of Mn^{2+} to Mn^{3+} is approximately 2.2 times higher than the enthalpy of oxidation of Mn^{3+} to Mn^{4+}. The estimated enthalpy of formation of the $La_{1-x}A_xMnO_{3-\delta}$, containing only Mn^{2+} becomes endothermic when the enthalpy of oxidation of Mn^{2+} to Mn^{3+} is 1.3 (for LCM) and 1.9 (for LSM) times higher than the enthalpy of oxidation of Mn^{3+} to Mn^{4+} for the ternary oxides. These calculations show that LCM and LSM probably become metastable with respect to the binary oxides (or other phases) when the concentration of Mn^{2+} becomes significant. Neglecting the effect of entropy, an endothermic enthalpy of formation will lead to decomposition of the materials.

$Ca_2Mn_2O_5$ and $Sr_2Mn_2O_5$ have successfully been prepared (43, 44). From the estimated enthalpy of formation discussed above, $La_2Mn_2O_5$ is unstable relative to La_2O_3 and MnO. However, solid solutions containing $La_2Mn_2O_5$ such as $LaCaMn_2O_5$ and $LaSrMn_2O_5$ might be stable. An exothermic enthalpy of formation is estimated for these materials based on an assumption that the enthalpy of oxidation of Mn^{2+} to Mn^{3+} is 2.2 times the enthalpy of oxidation from Mn^{3+} to Mn^{4+}. Here, the influence of the crystal structure is neglected.

Heterophase Interfaces in SOFC

The materials studied here are the most promising cathode materials in SOFC. The chemical stability of the interface between the cathode and the zirconia is one of the critical factors for the performance of the fuel cell. The reactions between ZrO_2 and $LaMnO_3$, $LaMnO_{3.148}$ (found in air at 993 K), and $AMnO_3$ (A = Ca and Sr) can be written as

$$2LaMnO_3 + 2ZrO_2 = Mn_2O_3 + La_2Zr_2O_7 \qquad [17]$$

$$2LaMnO_{3.148} + 2ZrO_2 = Mn_2O_3 + La_2Zr_2O_7 + 0.148O_2(g) \qquad [18]$$

$$2AMnO_3 + 2ZrO_2 = Mn_2O_3 + 2AZrO_3 + \tfrac{1}{2}O_2(g). \qquad [19]$$

The enthalpies of the reactions are − 16.0, − 2.3, 94.3 ($CaMnO_3$), and 63.5 ($SrMnO_3$) kJ/mol, respectively. The calculations are based on data reported in Fig. 1, enthalpies of formation of the $La_2Zr_2O_7$, $CaZrO_3$, and $SrZrO_3$ from binary oxides (45, 46), and enthalpies of formation of the binary oxides (27). Based on these data, the interface between ZrO_2 and $AMnO_3$ (A = Ca and Sr) are stable at low temperatures (strongly endothermic reactions). At 1273 K Mn_3O_4 is the stable phase in the Mn–O system. Substituting Mn_2O_3 with Mn_3O_4 in Eqs. [17]–[19] gives only endothermic enthalpies for the reactions between $LaMnO_3$, $LaMnO_{3.148}$, $CaMnO_3$, and $SrMnO_3$ and ZrO_2. The entropy for the reactions is presently unknown, but the mayor contribution is due to reduction of Mn from III (IV) to II. The entropy for the reduction of Mn_2O_3 to MnO (50 J/K per mole of Mn at 900 K (27)) represents a lower limit for the entropy.

Experimental studies of the heterophase interfaces LCM/CSZ and LSM/YSZ at temperatures between 1473 and 1625 K (47–50) have shown that the secondary phase $La_2Zr_2O_7$ is formed at low Ca and Sr contents. At high degree of Ca and Sr substitution in LCM and LSM, the secondary phases $CaZrO_3$ and $SrZrO_2$ were formed. The formation of the secondary phases can be represented by the reactions:

$$La_{1-x}A_xMnO_3 + \frac{y-x}{y} ZrO_2 = \frac{x}{y} La_{1-y}A_yMnO_3 + \frac{y-x}{2y} Mn_2O_3 + \frac{y-x}{2y} La_2Zr_2O_7 \quad [20]$$

$$La_{1-x}A_xMnO_3 + \frac{x-y}{1-y} ZrO_2 = \frac{1-x}{1-y} La_{1-y}A_yMnO_3 + \frac{x-y}{2(1-y)} Mn_2O_3 + \frac{x-y}{(1-y)} AZrO_3 + \frac{x-y}{4(1-y)} O_2(g). \quad [21]$$

The mass balances require that $x < y$ in Eq. [20] and $x > y$ in Eq. [21]. In these reactions the solubility of Mn in zirconia-based phases and the Y_2O_3 and CaO contents in ZrO_2 are neglected. The enthalpy for reaction [20] is exothermic at low x. However, the energetic driving force of the reaction decreased rapidly with increasing x. For the LSM system the enthalpy of the reaction became endothermic at lower x than in the LCM system (see Fig. 4). The enthalpy of reaction [21] is endothermic for all compositions, and the enthalpy increases with increasing x. These considerations show that the secondary phases $CaZrO_3$ and $SrZrO_3$ are not expected to be formed at low temperatures. $La_2Zr_2O_7$ is expected to form in materials with high La content. However, the present findings show that a careful investigation of the entropy of the involved phases is necessary in order to establish the equilibrium phase composition. The entropies of the solid solutions LCM and LSM are of particular importance here.

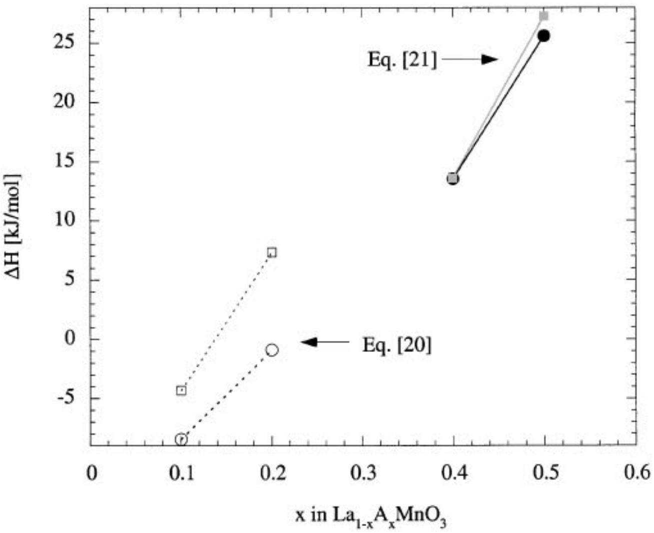

FIG. 4. Enthalpy of reactions [20] and [21] for $y = 0.3$ and $A = Sr$ (squares) and Ca (circles). Reaction [20] is shown as open symbols and dotted lines, while reaction [21] is given by filled symbols and solid lines.

In fired powder mixtures of $La_{0.6}Sr_{0.04}MnO_3$ and YSZ (8 mol% Y_2O_3) the observed secondary phase shifted from $La_2Zr_2O_7$ at 1473 K to $SrZrO_3$ at 1625 K (50). The observed shift was explained by the equation

$$La_2Zr_2O_7 + 2SrMnO_3 = 2SrZrO_3 + 2LaMnO_3 + \tfrac{1}{2}O_2(g). \quad [22]$$

The enthalpy of reaction [22] is 79.5 kJ/mol according to the present data (the corresponding value for reaction [22] with Ca instead of Sr is 100.3 kJ/mol). The endothermic enthalpy supports that the reaction is shifted to the right with increasing temperature due to a positive entropy (50).

CONCLUSIONS

The present study has shown that the exothermic enthalpy of formation of $La_{1-x}Ca_xMnO_{3\pm\delta}$ and $La_{1-x}Sr_xMnO_{3\pm\delta}$ from the binary constituents increases with increasing substitution of Ca and Sr. This can be understood in terms of the oxidation state of manganese which is going from Mn(III) to Mn(IV) with increasing alkali earth substitution. The enthalpy of formation for the perovskites is also observed to correlate well with the Goldschmidt tolerance factor as shown previously by Yokokawa *et al.* (41). The enthalpy of formation of $La_{1-x}Sr_xMnO_3$ is found to be higher than that for $La_{1-x}Ca_xMnO_3$ in line with the more basic nature of SrO compared to CaO. The $La_{1-x}Ca_xMnO_3$ solid solution behaves nearly as an ideal solid solution, while negative deviation from ideal solution is observed for the solid solution $La_{1-x}Sr_xMnO_3$. The enthalpy of oxidation of $LaMnO_{3+\delta}$ has been calculated from the measured enthalpy of formation of $LaMnO_{3.045}$ and $LaMnO_{3.148}$. The enthalpy of oxidation is significantly lower than the corresponding enthalpy of oxidation of $CaMnO_{3-\delta}$ and $SrMnO_{3-\delta}$ (20).

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