

REDOX THERMOCHEMISTRY OF $\text{SrFe}_{1-x}\text{Co}_x\text{O}_{3-\delta}$

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Abstract

The enthalpy of oxidation of $\text{SrFe}_{1-x}\text{Co}_x\text{O}_{3-\delta}$ with $x=0.33$ and 0.67 has been determined by adiabatic calorimetry; average values for $x=0.33$ and 0.67 are -67 ± 11 and -49.5 ± 9 kJ (mol O_2)⁻¹. These data and the previously reported value for $\text{SrFeO}_{3-\delta}$ suggest that the enthalpy of oxidation for pure (perovskite-type) $\text{SrCoO}_{3-\delta}$ is close to zero. Earlier reported composition – partial pressure data for $\text{SrFe}_{0.67}\text{Co}_{0.33}\text{O}_{3-\delta}$ are reproduced when preferential oxidation of iron is assumed for low partial pressures of oxygen.

Keywords: enthalpy of oxidation, perovskite, redox properties, $\text{SrFe}_{1-x}\text{Co}_x\text{O}_{3-\delta}$

Introduction

The redox energetics of a large group of complex non-stoichiometric perovskite-related oxides can be rationalized reasonably well through the use of a simple model description [1]. The main parameters of the model are the difference in enthalpy and vibrational entropy of formation between the two limiting compositions of the solid solution that corresponds to different formal oxidation states of the transition metal, and the configurational entropy due to a random distribution of the relevant species on the different sublattices. Aliovalent substitution is often used to modify and control the transport properties of the materials. In that respect the linear variation of the enthalpy of oxidation of $\text{La}_{1-x}\text{Ae}_x\text{TmO}_{3-\delta}$ (Ae =alkaline earth element, Tm =transition metal) with x observed for a number of systems with $\text{Tm}=\text{Mn}, \text{Co}, \text{Fe}$ makes estimates of the redox energetics simple [1]. The present contribution focuses on $\text{SrFe}_{1-x}\text{Co}_x\text{O}_{3-\delta}$; a perovskite-type oxide that recently has been much studied due to its mixed ionic and electronic conductivity [2] and due to its magnetoresistance near the Curie temperature [3]. The present study reports calorimetrically determined enthalpies of oxidation of $\text{SrFe}_{1-x}\text{Co}_x\text{O}_{3-\delta}$ for $x=0.33$ and 0.67 . The redox properties of $\text{SrFe}_{1-x}\text{Co}_x\text{O}_{3-\delta}$ are discussed.

The oxygen stoichiometry of $\text{SrFeO}_{3-\delta}$ and $\text{SrCoO}_{3-\delta}$ obtained on annealing at a given oxygen partial pressure and temperature show that Fe(III) is more easily oxidized to Fe(IV) than Co(III) to Co(IV). At $p_{\text{O}_2}=100$ GPa and $T=1373$ K, $\delta=0.08$ is obtained in the Fe-system, while $\delta=0.25$ in the Co-system [3] and the fully oxidized

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compounds are formed only on annealing at very high oxygen partial pressures [4, 5]. The perovskite-type phase with composition $\text{SrCoO}_{2.722}$ may be synthesized as a metastable product but tends to decompose according to [6]



$\text{Sr}_2\text{Fe}_2\text{O}_5$ and $\text{Sr}_2\text{Co}_2\text{O}_5$ are obtained on annealing at moderately reducing conditions [2, 7, 8].

The phase relations in the $\text{SrFe}_{1-x}\text{Co}_x\text{O}_{3-\delta}$ system are not well described in literature. In analogy with the $\text{SrFeO}_{3-\delta}$ system [9] ordered low-temperature phases with $\delta=0.5$, ≈ 0.25 , and ≈ 0.125 are found for $\text{SrFe}_{1-x}\text{Co}_x\text{O}_{3-\delta}$ with $x=0.1$, 0.2 and 0.3 [10]. Crystallographic [11] and thermogravimetric studies [12] of $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ show that even Co-rich compositions have ordered phases with $\delta=0.5$ and ≈ 0.25 at low temperatures. A grossly non-stoichiometric perovskite-type phase is stable at high temperatures [13,14] and the order-disorder transition is for $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_{2.50}$ observed near 1033 ± 20 K [11] compared to 1120 ± 5 K for $\text{SrFeO}_{2.50}$ [9]. Transformation temperatures are not reported for the other ordered low-temperature phases.

Experimental

Sample preparation and characterisation

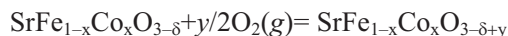
$\text{SrFe}_{1-x}\text{Co}_x\text{O}_{3-\delta}$ samples with $x=0.33$ and 0.67 were made by spray pyrolysis of metal nitrate solutions at Norsk Hydro AS, Porsgrunn, Norway. The resulting powders were ground in water for 30 min at 340 rpm in a planetary mill. The green bodies were further processed at University of Oslo. $\text{SrFe}_{0.67}\text{Co}_{0.33}\text{O}_{3-\delta}$ were calcined at 1123 K for 5 h, whereas $\text{SrFe}_{0.33}\text{Co}_{0.67}\text{O}_{3-\delta}$ were calcined at 1273 K for 10 h. The samples were subsequently reduced in 99.99 % $\text{N}_2(\text{g})$ at 1123 K for 20 h and cooled to room temperature with the furnace (approximate cooling rate 150 K h^{-1}).

The powder X-ray diffraction data were collected with a Siemens D5000, equipped with a primary Ge-monochromator and a position-sensitive detector, using CuK_α -radiation ($\lambda=154.0598 \text{ pm}$) radiation and Si as internal standard ($a=543.088 \text{ pm}$). Unit cell dimensions were determined by least-squares refinements using the UNITCELL program.

The oxygen content of the samples was determined by iodometric titration [15].

Reaction calorimetry

The step-wise heated adiabatic calorimeter and the measuring technique have been described earlier [16, 17]. The calorimeter is in the present case primarily used as a reaction calorimeter to determine the enthalpy of oxidation/reduction of perovskite-type $\text{SrFe}_{1-x}\text{Co}_x\text{O}_{3-\delta}$ according to



The temperature stability obtainable with accurate shield control makes adiabatic calorimeters ideal for the investigation of both energetic and kinetic aspects of

slow phase transformations [18]. In a step-wise heated adiabatic calorimeter the heat exchange with the surroundings is small and the temperature drift rate of the instrument is, thus, close to zero. Slow exothermal processes taking place in a sample give rise to small but significant positive temperature drift rate contributions in the equilibration periods. The temperature increment associated with an intermittent energy input is, hence, due to three effects; the electrically energy supplied, the heat exchange with the surroundings and the heat released by the sample. The enthalpy released from a sample is, hence, determined through

$$\Delta_{\text{sample}}H = \Delta_{\text{supplied}}H + \Delta_{\text{exch}}H - \Delta_{\text{total}}H \quad (1)$$

where the total enthalpy change of the calorimeter, $\Delta_{\text{total}}H$, from T_{start} to T_{final} is given as

$$\Delta_{\text{tot}}H = \int_{T_{\text{start}}}^{T_{\text{final}}} C_{\text{p,tot}} dT$$

Here $C_{\text{p,tot}}$ is the heat capacity of the calorimeter+sample. $\Delta_{\text{supplied}}H$ is supplied electrically by a constant current source. The current through the heater is measured every 10 s and the potential drop across the heater every second in between. The potential is measured using a 8½ digit Hewlett–Packard digital voltmeter. The current is determined by measuring the potential drop over a calibrated resistor. The total time, as well as the triggering of the potential and current measurements, are measured or controlled using a Keithley counter.

The heat exchanged with the surroundings is given by

$$\Delta_{\text{each}}H = \sum_{T_{\text{start}}}^{T_{\text{final}}} \frac{\Delta T}{\Delta t} \Delta t C_{\text{p,tot}}$$

where $\Delta T/\Delta t$ is the instrumental temperature-drift rate and Δt the time-interval of each step from T_{start} to T_{final} .

The samples are contained in open silica glass containers (40 cm³) that fits tightly into the calorimeter. A central well in the container serves for the heater and the platinum resistance thermometer. The calorimeter is heated in a step-wise fashion, and electrically heated and electronically controlled adiabatic shields surround the calorimeter proper. A guard shield system is outside the adiabatic shield and the whole assembly is placed in a vertical tube furnace. The calorimeter, shield, and guard are all made of silver.

The temperature was measured with an ASL F-18 resistance bridge using locally constructed 25 Ω platinum resistance thermometers. Temperature calibration is performed according to the recommendation of ITS-90 to 933.473 K. The accuracy in temperature determination is considered to be within ± 0.02 K. The temperature resolution is $\approx 3 \cdot 10^{-5}$ K [17].

Results and discussion

The unit-cell dimensions for the reduced samples ($\delta=0.5$) used in the calorimetric experiments [$x=0.33$; $a=5.633(3)$ Å, $b=15.644(5)$ Å, $c=5.504(2)$ Å; $x=0.67$; $a=5.600(2)$ Å, $b=15.678(8)$ Å, $c=5.493(3)$ Å] are in good agreement with literature values for $x=0.0$ [19] and $x=0.5$ [20], Fig. 1. The crystal structures of the oxidized samples are not known accurately and were analysed in terms of the structures re-

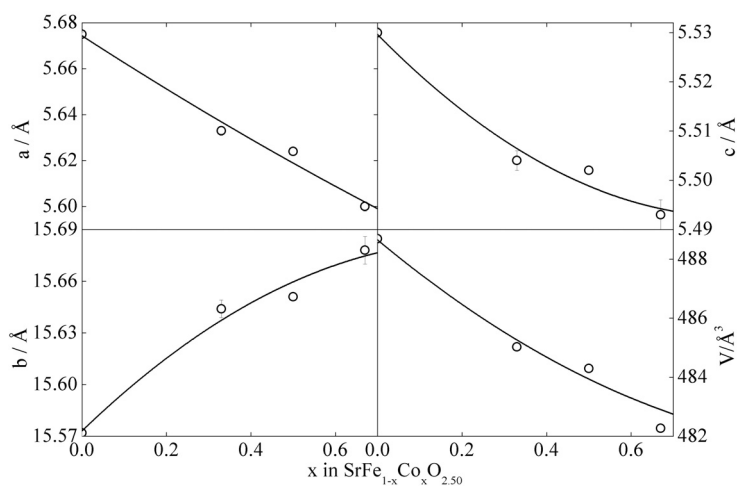


Fig. 1 Unit cell dimensions for $\text{SrFe}_{1-x}\text{Co}_x\text{O}_{2.50}$. Data points for $x=0.33$ and 0.67 present study; for $x=0$ Haavik *et al.* [9]; for $x=0.50$ Battle *et al.* [20]

Table 1 Calorimetric data for the two series of experiments on $\text{SrFe}_{1-x}\text{Co}_x\text{O}_{3-\delta}$ with $x=0.33$ and 0.67

	$x=0.33$		$x=0.67$	
	series I	series II	series I	series II
$T_{\text{start}}/\text{K}$	422.373	378.622	439.437	399.345
$T_{\text{final}}/\text{K}$	540.823	470.906	552.961	511.528
$\Delta_{\text{supplied}}H/\text{J}$	10465.8	8827.4	12167.5	8028.7
$\Delta_{\text{exch}}H/\text{J}$	5.5	175.8	-121.1	241.7
$\Delta_{\text{total}}H/\text{J}$	11540.8	10121.9	13470.4	8989.3
$\Delta_{\text{sample}}H/\text{J}$	-1069.5	-1118.6	-1424.0	-718.8
Mass increment/g	0.5344	0.5120	0.8416	0.5072

ported for $\text{SrFeO}_{3-\delta}$ with $\delta \approx 0.25$. All reflections could be indexed in terms of the rather large unit cell reported for $\text{Sr}_4\text{Fe}_4\text{O}_{11}$ [10].

Two determinations of the enthalpy of oxidation of samples with $x=0.33$ and 0.67 are reported. The temperature-drift rates observed during oxidation of $\text{SrFe}_{0.33}\text{Co}_{0.67}\text{O}_{3-\delta}$ (series I) are given (as an example) as function of temperature in Fig. 2. The reaction taking place in the calorimeter is

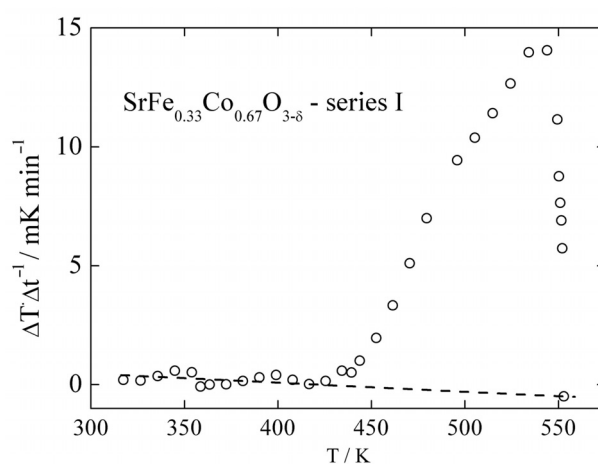
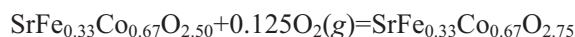


Fig. 2 Temperature drift rate observed during oxidation of $\text{SrFe}_{0.33}\text{Co}_{0.66}\text{O}_{2.50}$ (series I). Dashed curve represent the instrumental temperature-drift rate

The symbols represent the temperature-drift rates observed in the equilibrium-periods after each individual energy input. The dashed line gives the instrumental temperature-drift rate. This curve represent the average temperature drift rate observed in several series of separate experiments on non-reacting samples.

Table 2 Composition of calorimetric samples before and after oxidation and enthalpy of oxidation of $\text{SrFe}_{1-x}\text{Co}_x\text{O}_{3-\delta}$

Series	x	$3-\delta$		$\Delta_{\text{ox}}H/\text{kJ mol}^{-1}$
		Reduced sample*	Oxidized sample**	
I	0.33	2.544	2.840	-64 ± 9
II	0.33	2.546	2.687	-70 ± 12
I	0.67	2.499	2.734	-54 ± 7
II	0.67	2.501	2.752	-45 ± 10

* determined by chemical analysis

** determined from the mass increment during the calorimetric experiment

The calorimetric results are summarized in Table 1. The heat released by the sample, $\Delta_{\text{sample}}H$, is given by Eq. (1). $\Delta_{\text{total}}H$ is obtained by integration of the observed total heat capacity from T_{start} to T_{final} . $\Delta_{\text{suppl}}H$ is the electrically supplied energy, whereas $\Delta_{\text{exch}}H$ is determined from the observed instrumental temperature drift rate.

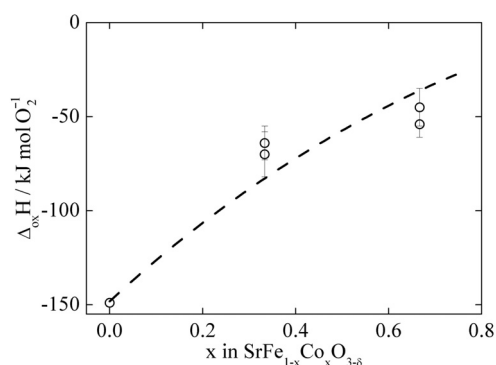


Fig. 3 Enthalpy of oxidation of $\text{SrFe}_{1-x}\text{Co}_x\text{O}_{3-\delta}$ as a function of mole fraction cobalt. Data for $x=0$ is taken from Bakken *et al.* [1]

The enthalpy of oxidation is determined from $\Delta_{\text{sample}}H$ and the corresponding oxygen consumption determined by using the mass increment of the calorimetric sample. The composition of oxidized and reduced samples determined by chemical analysis is used to verify the thermogravimetric analyses. The results are summarized in Table 2 and compared with the enthalpy of oxidation obtained for $\text{SrFeO}_{3-\delta}$ in Fig. 3. Extrapolation to $x=1$, i.e. pure $\text{SrCoO}_{3-\delta}$ give an enthalpy of oxidation close to zero. Co(III) is not easily oxidized to Co(IV).

The uncertainty given in the last column of Table 2 is estimated from the error induced by not correcting the experimental enthalpy of reaction for the heat capacity of reaction (the reaction takes place under non-isothermal conditions), the uncertainty of the instrumental temperature drift rate (judged to be 1 mK min^{-1}) and the uncertainty in the determination of the oxygen consumption during reaction.

Redox properties of $\text{SrFe}_{1-x}\text{Co}_x\text{O}_{3-\delta}$ ($0 \leq \delta \leq 1/2$)

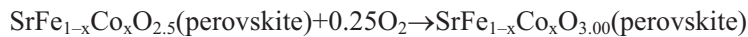
The redox process involves a simultaneous change in oxygen non-stoichiometry and in the formal valence state of iron/cobalt. In the simplest case $\text{SrFe}_{1-x}\text{Co}_x\text{O}_{3-\delta}$ ($0 \leq \delta \leq 1/2$) is seen as an ideal solid solution of two limiting compositions with different formal valence state $\text{SrFe}_{1-x}\text{Co}_x\text{O}_3$ and $\text{SrFe}_{1-x}\text{Co}_x\text{O}_{2.5}$ [1]. Fe(III), Co(III), Fe(IV) and Co(IV) are assumed to be randomly distributed on the iron sub-lattice while O^{2-} and $V_{\text{O}^{2-}}$ are assumed to be distributed randomly on the oxygen sub-lattice. The relationship between the partial pressure of oxygen, temperature and δ in $\text{SrFe}_{1-x}\text{Co}_x\text{O}_{3-\delta}$ is in this approximation

$$\log p_{O_2} = \frac{4}{RT \ln 10} [\Delta_f G^0(\text{SrFe}_{1-x}\text{Co}_x\text{O}_3) - \Delta_f G^0(\text{SrFe}_{1-x}\text{Co}_x\text{O}_{2.5})] - T \frac{\partial}{\partial x_0} (R \ln W)_{p,T,x} \quad (2)$$

The first term on right is in this ideal solution approach the Gibbs energy of oxidation

$$\Delta_f G^0(\text{SrFe}_{1-x}\text{Co}_x\text{O}_3) - \Delta_f G^0(\text{SrFe}_{1-x}\text{Co}_x\text{O}_{2.5}) \equiv \Delta_{ox} G^0 = \Delta_{ox} H^0 - T \Delta_{ox} S^0$$

that corresponds to the reaction



The ideal solution model implies that the enthalpy and entropy of oxidation is independent of composition and is thus compatible with the presently determined average enthalpy of oxidation of perovskite-type $\text{SrFe}_{1-x}\text{Co}_x\text{O}_{3-\delta}$.

The last term of Eq. (2) is the ideal partial configurational entropy of oxygen where

$$W = \frac{N_{BS}!}{N_{Co^{3+}}! N_{Co^{4+}}! N_{Fe^{3+}}! N_{Fe^{4+}}!} \frac{N_{OS}!}{N_O! N_V!}$$

N_{BS} and N_{OS} represent the number of B and O sites in ABO_3 , whereas N_V is the number of oxygen vacancies. Calculated stoichiometry – oxygen partial pressure isotherms at 1273 K are compared with experimental non-stoichiometry data in Fig. 4 ($\Delta_{ox} S = -125 \text{ J mol}^{-1} \text{ K}^{-1}$ [1, 9]). In the case of $x=0.33$ and 0.67 the average of the calorimetrically determined enthalpies of oxidation are used directly without considering possible contributions from order–disorder energetics. The XRD-data for the samples indicate that they are ordered at room temperature. No heat capacity anomalies indi-

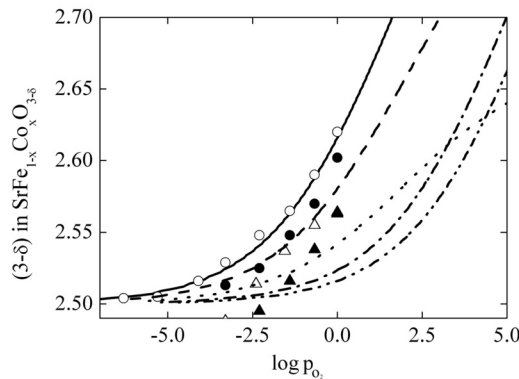


Fig. 4 $(3-\delta)$ in $\text{SrFe}_{1-x}\text{Co}_x\text{O}_{3-\delta}$ as a function of $\log p_{O_2}(g)$. Circles and triangles represent experiments for $x=0.0$ and 0.33 [2]. Open symbols *iso*- p_{O_2} experiments (T is varied); Closed symbols isothermal experiments (p_{O_2} is varied). —, --- and ····· represent calculations using Eq. (2) for $x=0, 0.33$ and 0.67 ; whereas the dashed and dotted curves represent calculations where iron is preferentially oxidized [Eq. (3)] for $x=0.33$ and 0.67

cating order–disorder transitions are observed on heating. Looking at the corresponding $\text{SrFeO}_{3-\delta}$ system, order–disorder transitions are observed but at temperatures higher than the present maximum temperatures. If we assume that both the reactants and the products are ordered the vacancy-ordering contribution will be a relatively small correction in the derivation of the enthalpy of oxidation of the disordered perovskite-phase. Hence, the directly measured enthalpies must be expected to give a reasonable first order estimate of the enthalpy of oxidation of perovskite-type $\text{SrFe}_{1-x}\text{Co}_x\text{O}_{3-\delta}$.

The experimental data obtained by varying the partial pressure of oxygen at constant temperature (closed symbols) and by varying temperature at constant partial pressure of oxygen (open symbols) are not in perfect agreement. The latter data are believed to be closer to equilibrium since the data points are obtained by cooling the samples from 1273 to 1073 K. The approach from high temperatures should reduce the effects of the lower temperature order–disorder transitions [21]. While the enthalpy of oxidation is in reasonable agreement with the equilibrium data for pure $\text{SrFeO}_{3-\delta}$ deviations are observed for $\text{SrFe}_{0.67}\text{Co}_{0.33}\text{O}_{3-\delta}$. Fe(IV) is more stable relatively to Fe(III) than Co(IV) relatively to Co(III). Hence, it may be argued that iron is preferably oxidized and that it is more reasonable to assume a random distribution of Fe(III), Fe(IV) and Co(III) on the B-lattice site at least at the more reducing conditions of the experiments performed by Holt *et al.* [2]. In that case $\log p_{\text{O}_2}$ is given by

$$\log p_{\text{O}_2} = \frac{4}{RT \ln 10} [\Delta_f G^0 (\text{SrFe}_{1-x}\text{Co}_x\text{O}_3) - \Delta_f G^0 (\text{SrFe}_{1-x}\text{Co}_x\text{O}_{2.5})] + 4[\log(1 - 2\delta) - \log(2\delta - x)] - 2 \log\left(\frac{\delta}{3 - \delta}\right) \quad (3)$$

This assumption leads to much better agreement between the calorimetric enthalpies of oxidation and the equilibrium data for $\text{SrFe}_{0.67}\text{Co}_{0.33}\text{O}_{3-\delta}$, Fig. 4. In these calculations the enthalpy of oxidation of Fe(III) is assumed to be independent of x in $\text{SrFe}_{1-x}\text{Co}_x\text{O}_{3-\delta}$ and the value for pure $\text{SrFeO}_{3-\delta}$ is used [1, 22]. This would lead to an apparent enthalpy of oxidation for the $x=0.33$ sample of -99 kJ mol^{-1} and for the $x=0.67$ sample of -50 kJ mol^{-1} . The latter is in perfect agreement with the calorimetric determination, the calorimetric value for $x=0.33$ is slightly low, -70 kJ mol^{-1} , in comparison.

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The samples were provided by Norsk Hydro AS.

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