A NOVEL CALORIMETRIC APPROACH TO THE REDOX THERMOCHEMISTRY OF NON-STOICHIOMETRIC OXIDES ENTHALPY OF OXIDATION OF $La_{1-y}Ca_yCrO_{3-\delta}$

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Abstract

A novel calorimetric approach to the energetics of redox reactions in non-stoichiometric oxides is presented. The method utilizes a step-wise heated adiabatic calorimeter for determination of average enthalpies of oxidation. The measurement uncertainty is dominated by the uncertainty in the determination of the mass increment due to the oxidation. An experimental investigation of the re-oxidation energetics of reduced $La_{1-y}Ca_yCrO_{3-\delta}$ is presented. The variation of the average formal oxidation state with temperature and oxygen fugacity is calculated from the experimentally determined enthalpy of oxidation and an estimated (lattice and configurational) entropy of oxidation. The calculated curves are in good agreement with experimental determinations reported in literature.

Introduction

The energetics of redox reactions in solid metal oxides is most often deduced from data obtained by equilibration methods, thermogravimetry or coulometric titration, or from electrical conductivity measurements. Direct calorimetric studies are also possible, and quite accurate determinations can be obtained by oxygen titration calorimetry and by solution calorimetry. The present paper introduces a new experimental approach to the redox thermochemistry of non-stoichiometric oxides. In certain metal oxides lower formal valence states of the metal are more stable at high temperatures and may furthermore be quenched to room temperature. If their kinetic stability in air is sufficiently high, the energetics of the re-oxidation reactions can be studied on heating the sample to some critical temperature in an adiabatic calorimeter.

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Oxides with perovskite-type related structure constitute an important class of compounds. Transition-metal oxides of this type often have extended non-stoichiometric ranges at high temperatures. The practical uses of these materials are in many cases related to the variable oxidation state of the metal, e.g. catalytic activity, superconductivity, and mixed ionic and electronic conductivity.

$LaCrO_3$ is not easily reduced or oxidized topotactically. However, when a fraction of the La^{3+} in $LaCrO_3$ is replaced with a divalent cation, the decrease in positive charge is compensated either by oxidation of Cr^{3+} to Cr^{4+} (formal oxidation numbers) or by formation of oxygen vacancies. Hence, specimens equilibrated in air at high temperatures contain Cr^{4+} (ideal composition $(La_{1-y}^{3+}M_y^{2+})(Cr_{1-y}^{3+}Cr_y^{4+})O_3$ where M is a divalent cation – Ca, Sr or Ba), whereas specimens reduced at low oxygen fugacities contain Cr^{3+} only and ideally have the composition $(La_{1-y}^{3+}M_y^{2+})Cr^{3+}O_{3-(y/2)}$. The variation of the average formal oxidation state of chromium with temperature and oxygen fugacity and the redox energetics have been studied for M=Ca by Yasuda and Hikita [1], for M=Sr by Mizusaki *et al.* [2], and for M=Mg in $LaCr_{1-y}Mg_yO_3$ by Flandermeyer *et al.* [3].

In the present study, the average enthalpy of oxidation of $La_{1-y}Ca_yCrO_{3-\delta}$ with y=0.20 and 0.30 was determined by adiabatic calorimetry. The uncertainty of the measured value and the possible sources of systematic errors are discussed. Experiments for a sample with y=0.10 are also considered. The average formal oxidation state of $La_{1-y}Ca_yCrO_{3-\delta}(0<\delta<y/2)$ is calculated as a function of temperature and oxygen fugacity.

Experimental

The preparation and characterization of the oxidized starting materials have been described elsewhere [4, 5]. Partly reduced samples were prepared by annealing in H_2/N_2 or CO/CO_2 mixtures at 873 to 1173 K for 5 to 8 h. The samples are unstable in air and a slight oxidation takes place even at room temperature [6]. The specimens were for that reason stored in vacuum desiccators until use. The compositons of the samples were deduced from the mass changes observed after reduction, after partial reoxidation in the calorimeter and after complete oxidation in an external furnace at 1070 K in air until constant mass. Phase analysis was made on selected reduced, partly reoxidized and completely reoxidized specimens by powder X-ray diffraction. Decomposition of a $La_{0.70}Ca_{0.30}CrO_3$ sample was observed once for a sample annealed in H_2/N_2. For all other specimens, no sign of decomposition or segregation of new phases at the grain boundaries was observed by X-ray diffraction nor by scanning electron microscopy.

The step-wise heated high-temperature adiabatic calorimeter and the measuring technique have been described elsewhere [7, 8]. 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 [9, 10]. In a step-wise heated adiabatic calorimeter the temperature drift rate of the instrument is close to zero, and slow exothermal processes give rise to small but significant positive

temperature drift rate contributions in the equilibration periods relatively to the background drift of the calorimeter. The temperature increment associated with an intermittent energy input is hence due to three effects; the electrically energy supplied, the instrumental temperature drift rate, and the heat released by the sample. The detection limit for heat effects due to slow phase transformations depends on the temperature stability of the instrument, i.e. to what extent the calorimeter approaches an adiabatic operation mode. Instrumental temperature drift rates of the order of 10^{-5} K s^{-1} are obtainable with our calorimeter under good experimental conditions even at high temperatures, $\approx$800 K. The sensitivity of the present calorimeter is, thus, high and heat effects of the order 1.5 mJ s^{-1} for a sample mass of around 150 g can be resolved. In the present experiments the sample mass used was around 35 g.

The uncertainty of an enthalpy of oxidation obtained by this method is to a large extent determined by the uncertainty in the determination of the mass increment. Since the reduced oxides are metastable in air at room temperature, the kinetics of the reoxidation reactions is a crucial factor, see below.

Results and discussion

The heat release due to oxidation of the reduced samples was detected by monitoring the temperature drift rate in the equilibration periods. In Fig. 1 the filled symbols show the temperature-drift rate after each individual energy input for reduced samples heated in air. The oxidation apparently starts near 340 K for all compositions and the highest reaction rates are observed at 440, 460 and 470 K for samples with y=0.10, 0.20 and 0.30. The temperature-drift rates observed in a second series of experiments on reoxidized samples are also shown, see open symbols in Fig. 1.
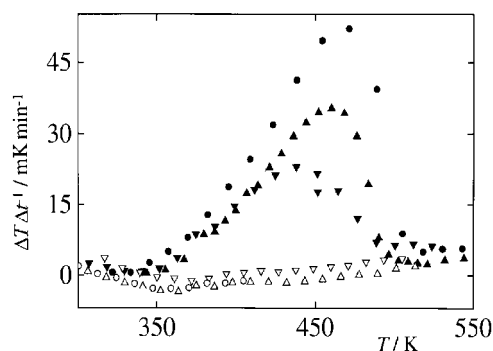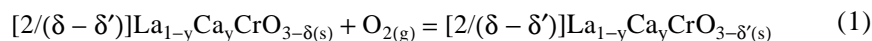

Fig. 1 The temperature drift rate for selected samples as a function of temperature of reduced (filled symbols) and oxidized (open symbols) La$_{1-y}$Ca$_y$CrO$_{3-\delta}$ with y=0.10 (inverse triangles), 0.20 (triangles) and 0.30 (circles)

The total temperature increment due to a series of intermittent energy inputs is due to three effects; the electrically supplied energy, the instrumental temperature-drift rate, and the heat released by the sample. The latter energy can be calculated since the two former contributions are determined independently in the second series

of experiment on the re-oxidized sample. The enthalpy of oxidation is then calculated from the heat released by the sample and the corresponding mass increment.

The average enthalpy of oxidation determined from four series of determinations on samples with $y=0.20$ and 0.30 for reaction (1) is $\Delta_r H_m = -500 \pm 50$ kJ mol^{-1}.

$$[2/(\delta - \delta')]La_{1-y}Ca_yCrO_{3-\delta(s)} + O_{2(g)} = [2/(\delta - \delta')]La_{1-y}Ca_yCrO_{3-\delta'(s)} \qquad (1)$$

In the experiments, $3-\delta$ in $La_{1-y}Ca_yCrO_{3-\delta}$ varied from 2.920 to 2.983 and from 2.962 to 2.985 for $y=0.20$ and from 2.875 to 2.969 and from 2.882 to 2.969 for $y=0.30$. The uncertainty for the present determination is relatively large and estimated to be near 10%. The main source of uncertainty is the slow oxidation taking place already at room temperature.

Although the unfavorable kinetics of the re-oxidation reactions gives a 10% uncertainty for our determination, the enthalpy of oxidation is in reasonable agreement with values deduced from thermogravimetric and transport property measurements, Fig. 2. In order to obtain the variation of the enthalpy of oxidation with the La to Ca ratio a larger number of experiments must be carried out for each composition. Still, our experiments indicate an increase in the enthalpy of oxidation with increasing Ca^{2+} content. The determinations by Mizusaki *et al.* [2] for Sr substituted $LaCrO_3$ concur, whereas the values reported by Flandermeyer *et al.* [3] for Mg substituted samples show an opposite trend. The only earlier reported value for Ca^{2+} doped $LaCrO_3$ [1] is in very good agreement with the present result. It should be noted that while Mizusaki *et al.* [2] report a significant variation of the enthalpy of oxidation with the degree of non-stoichiometry, we have averaged his values to make a comparison with the presently measured average enthalpy of oxidation possible.
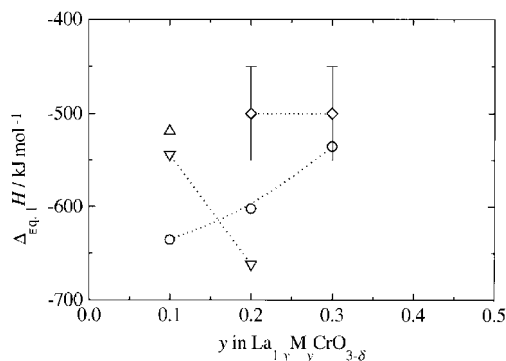

Fig. 2 Enthalpies of oxidation of Cr^{3+} to Cr^{4+} in $La_{1-y}M_yCrO_{3-\delta}$. Present determinations (diamonds) for M=Ca and experimental determinations by Yasuda and Hikita (triangles) for M=Ca [1]; by Mizusaki *et al.* (circles) for M=Sr [2]; and by Flandermeyer *et al.* (inverse triangles) for M=Mg [3]

In cases where the metastable reduced oxides are more stable in air, a much lower uncertainty is obtained. As an example, the oxidation of $Sr_2Fe_2O_5$ (or $SrFeO_{2.5}$) to $Sr_8Fe_8O_{23}$ ($SrFeO_{2.875}$) is considered. The uncertainty is mainly due to the uncer-

tainty in mass increase on oxidation and for $Sr_2Fe_2O_5$ thermogravimetric analyses indicate that the mass increase can be determined with an uncertainty less than 3%. A preliminary value of the mean enthalpy of oxidation at temperatures near 650 K for the reaction

$$4Sr_2Fe_2O_{5(s)} + 3/2O_{2(g)} = Sr_8Fe_8O_{23(s)}$$
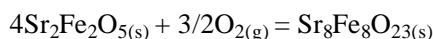
evaluated from two series of measurements, is $\Delta_r H_m = -172 \pm 6$ kJ mol^{-1} [11]. In order to obtain this low uncertainty the calorimetric experiments must be combined with accurate thermogravimetry. This is because the average formal oxidation state, given by δ in $SrFeO_{3-\delta}$, varies considerably with temperature and oxygen fugacity even at the low temperatures where the experiments are performed [11]. The low uncertainty for the enthalpy of oxidation compares in this case favorably with the uncertanity obtained from equilibration studies and from solution and titration calorimetry.

An obvious reason for our interest in the redox thermochemistry is that the energetic parameters may enable us to estimate the average formal oxidation state, i.e. the oxygen non-stoichiometry, of a complex oxide as a function of temperature and oxygen fugacity. The Gibbs energy of formation $La_{1-y}M_yCrO_{3-\delta}$ can be expressed by modelling the phase as a solution of the two ordered compounds [12]: $La_{1-y}M_yCrO_{3-y/2}$ and $La_{1-y}M_yCrO_3$. The former compound contain Cr^{3+} only whereas the latter has the maximum amount of Cr^{4+} given by the La to M ratio. The Gibbs free energy of formation of $La_{1-y}M_yCrO_{3-\delta}$ is given by [12]:

$$\Delta_f G(La_{1-y}M_yCrO_{3-\delta}) = (1-x)\Delta_f G(La_{1-y}M_yCrO_3) - x\Delta_f G(La_{1-y}M_yCrO_{3-y/2}) +$$

$$+ RT[(1+yx-y)\ln(1+yx-y) + (y-yx)\ln(y-yx) + (xy/2)\ln(xy/6) +$$

$$+ (3-(xy)/2)\ln(1-(xy)/6)]$$

where δ is related to x, the mole fraction of the reduced compound. The partial Gibbs free energy of oxygen can be expressed as a function of y and δ in $La_{1-y}M_yCrO_{3-\delta}$ as

$$\log p_{O_2}(atm) = [4/(yRT\ln 10)][\Delta_f G(La_{1-y}M_yCrO_3) - \Delta_f G(La_{1-y}M_yCrO_{3-y/2})] +$$

$$+ 2\log[\{(3-\delta)/\delta\}\{(y-2\delta)/(1-y+2\delta)\}^2]$$

where the latter term is the configurational entropy (due to mixing of Cr^{3+} and Cr^{4+} and of O^{2-} and V_O^{2-}) and the former term is the difference between the Gibbs energy of formation of the reduced and oxidized compounds. The difference in enthalpy of formation is based on the presently determined enthalpy of oxidation, whereas the entropy is estimated. The experimentally determined entropy for $LaFeO_3$ [13] is used for the oxidized compounds, whereas a zeroth order estimate of the entropies of the reduced compounds is obtained simply by taking the number of atoms into consideration.

The average formal oxidation states at 1273 K, expressed as $(3-\delta)$ of $La_{1-y}M_yCrO_{3-\delta}$, for samples with $y=0.10$, 0.20 and 0.30 are presented in Fig. 3. The effect of temperature on the non-stoichiometry of the $y=0.30$ composition is also shown. The presently estimated values (for M=Ca) given by lines are in quite reasonable agreement with the experimental determinations by Mizusaki et al. for M=Sr [2]. For the sample with $y=0.10$ the experimental results [2] seem to indicate a more negative enthalpy of oxidation than for $y=0.30$. $\Delta_{Eq.(1)}H$ of the order of -550 kJ mol^{-1} gives a reasonable curve.
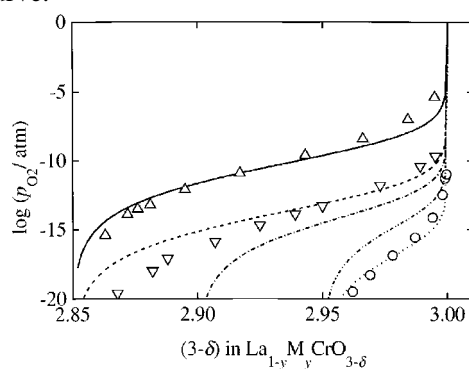

Fig. 3 Oxygen non-stoichiometry as a function of temperature and oxygen fugacity for $La_{1-y}M_yCrO_{3-\delta}$. The symbols represent experimental determinations for M=Sr by Mizusaki et al. [2]; T=1573 K and $y=0.30$ (triangles); T=1273 K and $y=0.30$ (inverse triangles) and T=1273 K and $y=0.10$ (circles). The lines represent the present calculations for M=Ca; T=1573 K and $y=0.30$ (—); T=1273 K and $y=0.30$ (- - -), 0.20 (- · · -) and 0.10 (· · · and - · · -). The entropy of oxidation for Eq. (1) used at 1573 K is -116 J K^{-1}mol^{-1} and at 1273 K is -120 J K^{-1}·mol^{-1}. For the dotted line the enthalpy of oxidation is -550 kJ mol^{-1}, in all other cases -500 kJ mol^{-1}

Concluding remarks

It seems that relatively simple calorimetric determinations of the average enthalpy of oxidation of non-stoichiometric oxides enable reasonable estimates of the redox properties. The present calorimetric technique is applicable to certain types of oxides only. The reduced sample must be kinetically stable in air at ambient conditions and reoxidize within some few hours at temperatures below 800 K. Our statistical model assumes randomly distributed species on the different sub-lattices. Preliminary results for the entropy of order-disorder transitions in the $Sr_2Fe_2O_5$–$SrFeO_3$ system, suggest that the defects in the high-temperature phase are far from randomly distributed [11] at least close to the order-disorder transition temperature. Similar results have been obtained by Prasanna and Navrotsky for $Ba_2In_2O_5$ where the entropy of the order-disorder transition is less than 10% of that expected for complete randomization of the brownmillerite-like structure [14]. O^{17} NMR experiments suggest that oxygen become mobile first within the tetrahedral layers at the order-disorder transition studied calorimetrically (1198 K) and completely random only when the

structure turns cubic at 1348 K [15]. The latter transition is of second order and the disorder appears to increase slowly with temperature. Hence, some hundred degrees above the transition temperature, random order seems to be a reasonable assumption in that particular system. The present results suggest that the defects in $La_{1-y}M_yCrO_{3-\delta}$ also are randomly distributed.

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