Thermochemistry of Perovskite-related oxides with high oxidation states: Superconductors, sensors, fuel cell materials

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Abstract: Perovskite-related oxides containing transition metals (Mn, Fe, Co, Ni, Cu) in high formal oxidation states are important materials as high temperature superconductors, electrochemical sensors and solid oxide fuel cell electrodes. High oxidation states are stabilized by large alkaline earth ions, Ba and Sr. Recent study by high temperature reaction calorimetry has revealed systematics in both enthalpies of formation and of oxygen incorporation in these materials. The enthalpy of formation from the oxides of a series of ternary oxides containing formal Cu^{3+} becomes increasingly exothermic with decreasing ionic potential, charge/size, of the counterbalancing cation, that is, in the series $LaCuO_3$, $LaSrCuO_4$, $LaBaCuO_4$, $NaCuO_2$, $KCuO_2$. The enthalpy of oxygen incorporation becomes more exothermic in the sequence M = Ca, Sr, Ba for the series $M_xLa_{2-x}CuO_{4-y}$. The oxidation enthalpy is similar for Ba-doped lanthanum cuprates and for YBCO. This enthalpy is similar to that of the formation of the corresponding alkaline earth peroxide for both Ba and Sr, suggesting an energetic and possibly also structural relation between hole states in these multicomponent oxides and in peroxides. The doped lanthanum nickelates and cobaltates show more exothermic oxidation energetics than the cuprates. The overall energetics are governed by the competition of oxygen vacancy formation, oxidation to formal M^{3+}, and coupled ionic substitution. Energetic parameters for these defect formation reactions are derived from calorimetric data.
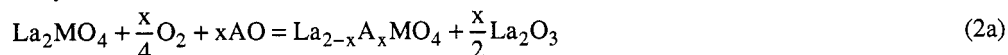
Introduction

Perovskite-related oxides figure prominently as ceramics, piezoelectrics, electrodes for oxide fuel cells, superconductors, and minerals in the Earth's lower mantle. The ubiquitous occurrence and varied electronic and transport properties of these materials reflect the perovskite structure's unique ability to tolerate defects of various sorts - ions of different sizes accommodated by distortional phase transitions, various stoichiometry accommodated by intergrowths, layered structures, and both ordered and disordered arrangements of cation and anion vacancies, and electronic defects assisted by covalency, delocalization, and the unique matching of cation and anion electronic bands. Clearly this extreme flexibility in structure, composition, and properties is related to unique thermodynamic behavior, some aspects of which are explored in this paper.

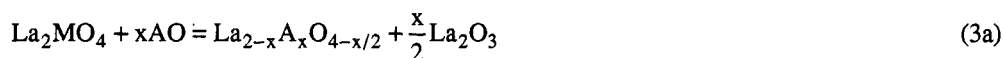## Energetics of High Oxidation States in Doped Lanthanum Cuprates, Nickelates, and Cobaltates, $La_{2-x}A_xMO_{4-y}$

The K_2NiF_4 structure is seen in La_2CuO_4, La_2NiO_4, and La_2CoO_4. In the pure phases and when these oxides are doped with a divalent alkaline earth, three types of defect reactions are in competition. The first is oxidation with the incorporation of oxygen interstitials and an oxygen content, y > 4.00

$$La_2MO_4 + (y/2)O_2 = La_2MO_{4+y} \tag{1a}$$

$$2M_M^{2+} + 1/2O_2 = 2M_M^{3+} + O_I^{2-} \tag{1b}$$

$$null = 2h_M' + O_I'' \tag{1c}$$

The second is oxidation of M^{2+} balanced by substitution of A^{2+} for $La^{3+,}$ and no change in oxygen stoichiometry

$$La_2MO_4 + \frac{x}{4}O_2 + xAO = La_{2-x}A_xMO_4 + \frac{x}{2}La_2O_3 \tag{2a}$$

$$La_{La}^{3+} + M_M^{2+} = A_{La}^{2+} + M_M^{3+} \tag{2b}$$

$$null = A_{La}^{\cdot} + h_M' \tag{2c}$$

The third is creation of oxygen vacancies, rather than oxidation, to charge compensate the substitution of divalent for trivalent A-site cations

$$La_2MO_4 + xAO = La_{2-x}A_xO_{4-x/2} + \frac{x}{2}La_2O_3 \tag{3a}$$

$$2La_{La}^{3+} + O_O^{2-} = 2A_{La}^{2+} + V_O \tag{3b}$$

$$null = 2A_{La}^{\cdot} + V_O'' \tag{3c}$$

Furthermore, the oxygen vacancies, when created in substantial concentrations, can form an order structure.

Recent calorimetric studies (1-4) have enabled the separation of the energetics of these processes for M = Cu, Ni, Co and A = Ba, Sr, Ca, Pb (see Table 1).

TABLE 1. Enthalpies (kJ/mol) of various reactions in the $La_{2-x}A_xMO_{4-y}$ oxides (data from Ref. 1-4, 6, 7, 9, 10).

Compound	Formation of stoichiometric compound	Oxidation (per O)		Coupled substitution with vacancy formation	Vacancy ordering
		$y>0$ vacancy regime	$y<0$ interstitial regime		
La_2CuO_4	-19.3±1		~0		
$La_{2-x}Ba_xCuO_{4-y}$		-110±25		0±10	-110±20
$La_{2-x}Sr_xCuO_{4-y}$		-65±10		0±10	-40±10
$La_{2-x}Ca_xCuO_{4-y}$				0±10	8±10
La_2NiO_4	2.2±5				
$La_{2-x}Ba_xNiO_{4-y}$		-148±18	-105±5		
$La_{2-x}Sr_xNiO_{4-y}$			-105±5		
La_2CoO_4	-40±5				
$La_{2-x}Sr_xCoO_{4-y}$					
$YBa_2Cu_3O_7$	-118±10	-95±3			
$BaNiO_2$	-32.0±5		-98±10		

The enthalpy of formation of $La_{2-x}A_xCuO_{4-x/2}$ (A = Ba, Sr, Ca, and Pb) from component oxides, represented by:

$$(1-x/2)\ La_2O_3 + x\ AO + CuO \rightarrow La_{2-x}A_xCuO_{4-x/2} \tag{4}$$
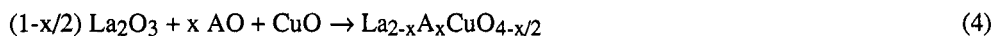
is shown in Figure (1a) as a function of divalent ion concentration. The reaction represents formation of a compound with no extrinsic holes (or electrons). The acceptors are completely compensated by oxygen vacancies. Such a compound could be oxidized, all the oxygen vacancies filled, with the generation of extrinsic holes. The formation of material with a fully occupied oxygen (and cation) lattice (the fully oxidized compound) from component oxides can be represented as follows:

$$(1-x/2)\ La_2O_3 + x\ AO + x/4\ O_2 + CuO \rightarrow La_{2-x}A_xCuO_4 \tag{5}$$
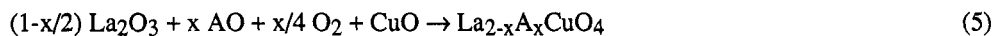
The difference between the enthalpy these two reactions is the enthalpy of oxidation of $La_{2-x}A_xCuO_{4-y}$, -65 kJ/mol of O for Sr doped materials and -105 kJ/mol of O for Ba doped materials. The formation of fully oxidized doped lanthanum cuprate can also be represented as:
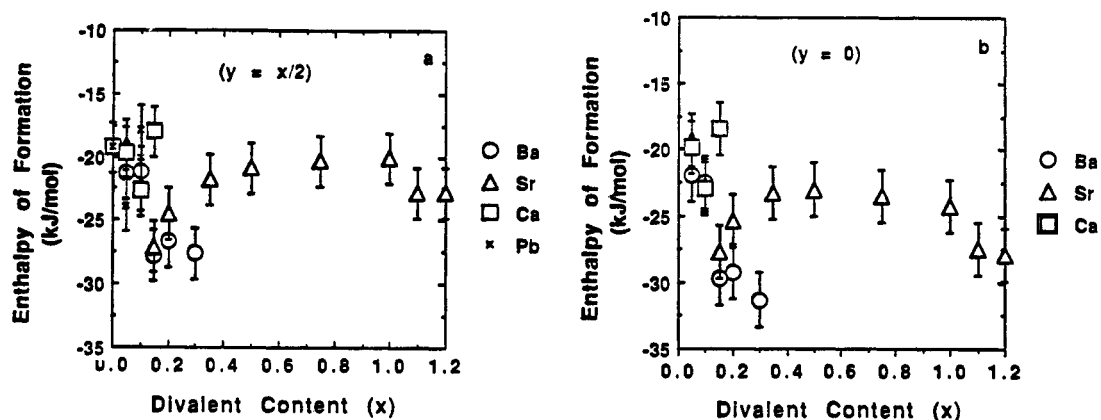
Fig. 1   (a)   Enthalpy of reaction
$(1 - x/2)La_2O_3 + xAO + CuO =$
$La_{2-x}A_xCuO_{4-x/2}$

            (b)   Enthalpy of reaction
$(1 - x/2)La_2O_3 + (x/2)AO$
$+ (x/2)AO_2 + CuO = La_{2-x}A_xCuO_4$

$$(1-x/2) La_2O_3 + x/2 AO + x/2 AO_2 + CuO \rightarrow La_{2-x}A_xCuO_4 \qquad (6)$$

This represents a formation reaction free of gaseous species. Figure (1b) shows the enthalpy of formation of $La_{2-x}A_xCuO_4$ from the component oxides and peroxides as a function of the acceptor concentration. Figures 1a and 1b are almost identical. The enthalpy of oxidation of $La_{2-x}A_xCuO_{4-y}$ is very similar to the enthalpy of oxidation of the corresponding alkaline oxide (AO) to the alkaline peroxide, given by:

$$AO + 1/2 \, O_2 \rightarrow AO_2 \qquad (7)$$

with $\Delta H = -55$ kJ/mol for SrO_2 and -85 kJ/mol for BaO_2.

Oxidation reactions in a crystal can be written in a generic form as:

$$1/2 \, O_2 \, (gas) \rightarrow O^{2-} \, (crystal) + 2 \, h \, (crystal) \qquad (8)$$

This process has two parts. The first part involves accommodation of the oxygen anion in the crystalline structure. In $La_{2-x}A_xCuO_{4-y}$, oxygen fills a basal vacancy which is presumably in the vicinity (to maintain local electroneutrality) of an alkaline earth acceptor. Therefore, in the process of oxidation of AO as well as $La_{2-x}A_xCuO_{4-y}$, the oxygen ion is near an alkaline earth cation. The separation of the alkaline earth cation and the entrant oxygen is very similar in AO_2 and in $La_{2-x}A_xCuO_{4-y}$. This suggests that energetically the process of oxygen ion accommodation can be expected to be very similar in AO (forming AO_2) and $La_{2-x}A_xCuO_{4-y}$ (5).

The other part of oxidation involves the accommodation of holes in the crystalline structure. The holes in an alkaline-earth peroxide are localized in bonds between the two adjacent oxygens, the peroxide bonds. As energetically the overall process of oxidation and the process of accommodation of the anions in AO and $La_{2-x}A_xCuO_{4-y}$ is similar; the process of accommodation of holes must be energetically similar. The holes in $La_{2-x}A_xCuO_{4-y}$ are, thus, energetically, in peroxide like bonding states (5). We also see structural evidence in terms of shortened O-O distances for incipient peroxide formation; for details see Mehta et al. (5).

Many transition metals (M = Fe, Co, Ni and Cu) form La_2MO_4 compounds with the K_2NiF_4 structure which over most of their stability field they p-type materials. The energetics of cuprates, nickelates, and cobaltates, can be meaningfully compared. Figure 2 shows one such comparison, namely of the enthalpy of formation of the stoichiometric (y = 0) compounds from the component oxides. The enthalpy of formation for La_2NiO_4 is very close to zero (2.2 ± 5 kJ/mole), whereas La_2CuO_4 is substantially exothermic (-19 ± 1 kJ/mol). The close to zero enthalpy of formation of $La_2NiO_{4.00}$ and the strongly exothermic enthalpy of oxidation may explain why this phase, under normal synthetic conditions, is highly oxygen rich ($La_2NiO_{4.18}$ at 973 K in air) and is very difficult to synthesize stoichiometric.

In $La_{2-x}Sr_xCoO_{4-y}$ only K_2NiF_4 phases that are fairly heavily Sr-doped can be synthesized, namely $0.6 \leq x \leq 1.5$. These appear to be oxygen deficient (0 < y < 0.5), depending on oxygen fugacity. Correcting measured enthalpies of formation of nearly fully oxidized materials to y = 0, the heats of formation of

$La_{2-x}Sr_xCoO_4$ shown in Figure 2 are obtained. The enthalpy of formation of La_2CoO_4 is estimated to be -40 kJ/mol, which makes it energetically more stable with respect to binary oxides than either La_2NiO_4 or La_2CuO_4. The nonexistence of La_2CoO_4, therefore, implies a greater stability for $LaCoO_3$ perovskite, not an absolute instability for the K_2NiF_4-type material.

The enthalpy of oxidation in the vacancy regime become mores exothermic (for A = Sr) in the series Cu, Ni, Co, with values of -65, -148 and -200 kJ/mol respectively (per one oxygen).

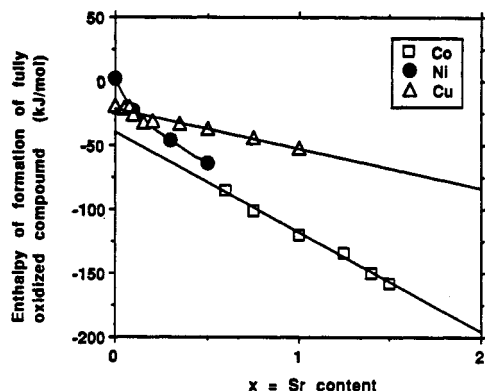Fig. 2   Enthalpy of reaction
$(1 - x/2)La_2O_3 + xSrO$
$+MO + (x/4)O_2 = La_{2-x}Sr_xMO_4$
(Calculated from data in ref. 1-4).

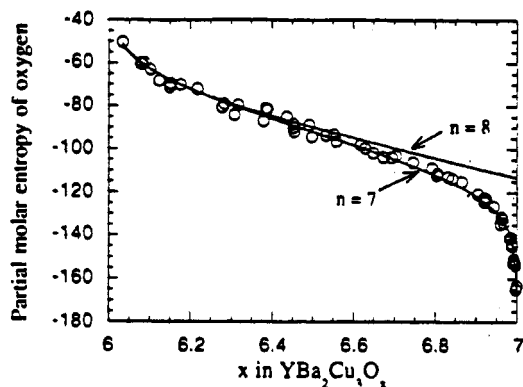Fig. 3   Partial molar entropy ($J\ mol^{-1}\ K^{-1}$) of oxygen solution in the 123 structure $\Delta\bar{s}_O$ vs oxygen content x in $YBa_2Cu_3O_x$, n = 7 refers to the preferred configurational entropy model with 7 oxygen sites per unit, and n = 8 refers to a model with 8.

YBCO Phases
High temperature reaction calorimetry has been done on $YBa_2Cu_3O_{7-x}$ and related phases in the Y-Ba-Cu-O system (6). Analysis of the oxidation state of Cu in lead borate indicates that the reaction during drop solution calorimetry is:

$$YBa_2Cu_3O_x\ (298\ K) + (6.5-x)/2\ O_2\ (g, 975\ K)$$
$$= \{1/2\ Y_2O_3 + 2\ BaO + 3\ CuO\}\ (soln, 975\ K) \tag{9}$$
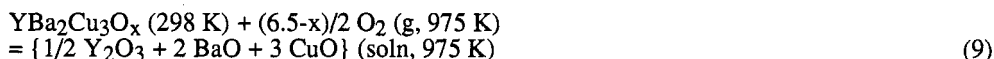
Data for the same system were obtained previously (7) by transposed temperature drop calorimetry to 1057 K. Both show a linear dependence of enthalpy on oxygen content, x, and give a partial molar enthalpy of oxygen (oxidation enthalpy), $\Delta\bar{h}_O = -101 \pm 5.5\ kJ\ mol^{-1}$ per O (drop solution calorimetry) and $\Delta\bar{h}_O = -95 \pm 2$ kJ/mol (transposed temperature drop calorimetry). The intercalation of oxygen is exothermic and energetically stabilizes structures with higher oxygen contents. The constancy of $\Delta\bar{h}_O$ with composition implies that the oxygen energetics are insensitive to the orthorhombic-tetragonal transition and that the distribution of valence states changes continuously, with no titration end-point at x = 6.5.

In contrast, the partial molar entropy of oxygen absorption, calculated by combining the above enthalpy with free energy data, (8), shows a sigmoid variation with x, consistent with a simple configurational entropy and a linearly varying nonconfigurational entropy across this solid solution series, (see Figure 3).

Measured enthalpies of formation of $YBa_2Cu_3O_x$ and related phases are listed in Table 2. Large exothermic enthalpies of formation from simple oxides are due to the basicity of BaO. $Y_2Cu_2O_5$ has a small endothermic enthalpy of formation from the oxides, implying that it is entropy-stabilized.

TABLE 2. The enthalpies of formation of $YBa_2Cu_3O_x$ and related phases from oxides and from elements (data from ref. (6))

Compound	ΔH_f (kJ/mol)	
	from oxides	from elements
$YBa_2Cu_3O_x$ (295 K)		
x = 6.33	-79.4 ± 7.3[a]	-2575 ± 9
x = 6.45	-76.8 ± 4.9[a]	-2590 ± 7
x = 6.48	-74.1 ± 6.1[a]	-2592 ± 8
x = 6.64	-86.8 ± 7.2[b]	-2608 ± 9
x = 6.87	-101.8 ± 6.4[b]	-2623 ± 9
x = 6.92	-110.3 ± 9.5[b]	-2631 ± 11
Y_2BaCuO_5 (295 K)	-52.9 ± 3.0[c]	-2664 ± 5
Y_2BaCuO_5 (975 K)	-59.3 ± 3.0[c]	
$Y_2Cu_2O_5$ (295 K)	$+9.2 \pm 3.2$[c]	-2211 ± 5
$Y_2Cu_2O_5$ (975 K)	$+6.6 \pm 2.9$[c]	
$BaCuO_{2.01}$ (295 K)	-83.8 ± 3.1[b]	-789 ± 4
$YBa_2Cu_4O_8$ (295 K)	-145.8 ± 10.4[b]	-2824 ± 12

a. from BaO, Y_2O_3, CuO and Cu_2O
b. from BaO, Y_2O_3, CuO and O_2
c. from BaO, Y_2O_3, CuO

These data have been used to discuss phase equilibria in the $BaO-Y_2O_3-Cu-O$ system, to analyze the stability fields of the 123, 124, and 247 compounds (6, 8).

Other Compounds

The enthalpies of formation from the oxides of $KCuO_2$, $NaCuO_2$, $BaLaCuO_4$, $SrLaCuO_4$ and $LaCuO_3$ are shown in Figure 4 plotted against the ionic potential (z/r) of the large A-site cation. The enthalpy of formation, and therefore the stabilization of the high oxidation state of copper, becomes increasing exothermic with decreasing z/r, i.e. increasing basicity of the A-site cation, as has been generally assumed.

Materials with potential oxide fuel cell applications (as electrodes and interconnects) and as mixed electronic/ionic conductors include perovskites of the $LaCrO_3$, $LaMnO_3$, $LaFeO_3$, $LaCoO_3$, and $LaNiO_3$ types, including solid solutions among these and phases with other rare earth substitutions. They need to be stable over a wide range of temperatures and oxygen fugacities, with conditions from air to strongly reducing fuel mixtures. Their thermodynamic properties are incompletely known and a calorimetric study along the lines of that described above for La_2MO_4 phases is being initiated. The perovskite phases dominate over the La_2MO_4 phases when high oxidation states (M^{3+}, M^{4+}) are relatively stable with respect to M^{2+}, that is, earlier in the transition series, namely for M = Cr, Mn, Fe, Co. The enthalpies of formation, of oxidation, and of defect formation need to be determined. These thermodynamic data will define phase compatibility between these perovskites, zirconia-based solid electrolytes, metals, and fuel gases.

The brownmillerite structure is a vacancy-ordered perovskite type seen in $Ca_2Fe_2O_5$. The $Ca_2Fe_2O_5$-$CaTiO_3$ system contains a family of ordered intergrowth structures based on complex ordered perovskites. The enthalpies of some of these have been determined (11), see Figure 5. The intermediate compounds are the same or slightly less stable in enthalpy than the end-members, suggesting that entropy (from disordered Fe, Ti distributions) rather than energy, is the reason for their stability, and that they might be unstable at low temperature.
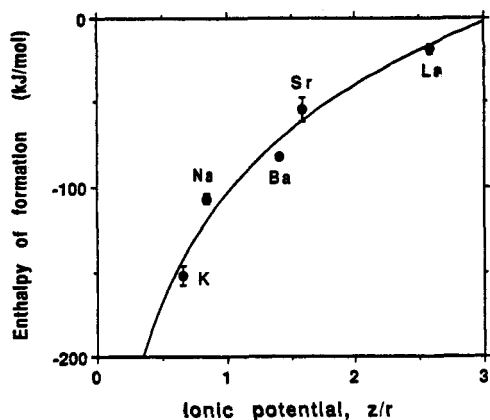
Fig. 4   Enthalpy of formation for oxides of compounds; K = $KCuO_2$, Na = $NaCuO_2$, Ba = $BaLaCuO_4$, Sr = $SrLaCuO_4$, La = $LaCuO_3$ (from Ref. 2, 10 and unpublished data).
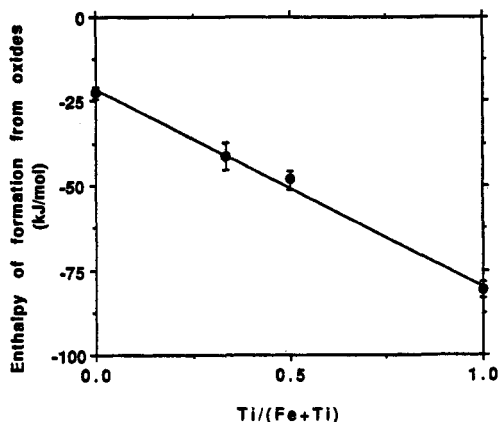
Fig. 5   Enthalpy of formation from oxides of compounds along the $Ca_2Fe_2O_5$ - $Ca_2Ti_2O_6$ join (11).

REFERENCES

1.   J. Bularzik, A. Navrotsky, J. DiCarlo, J. Bringley, B. Scott, and S. Trail. *J. Solid State Chem.*, **93**, 418 (1991).
2.   J. DiCarlo, J. Bularzik and A. Navrotsky. *J. Solid State Chem.*, **96**, 381 (1992).
3.   J. DiCarlo, A. Mehta, D. Banschick, and A. Navrotsky. *J. Solid State Chem.*, **103**, 186 (1993).
4.   T.R.S. Prasanna and A. Navrotsky. *J. Solid State Chem.* (in press).
5.   A. Mehta, J. DiCarlo, and A. Navrotsky. *J. Solid State Chem.*, **101**, 173 (1992).
6.   Z. Zhou and A. Navrotsky. *J. Mater. Res.*, **7**, 2920 (1992).
7.   M.E. Parks, A. Navrotsky, K. Mocala, E. Takayama-Muromachi, A. Jacobson and P.K. Davies. *J. Solid State Chem.*, **79**, 53 (1989), Erratum **83**, 218 (1989).
8.   Z. Zhou and A. Navrotsky. *J. Mater. Res.* (in press).
9.   J. DiCarlo, I. Yazdi, A. J. Jacobson, and A. Navrotsky. *J. Solid State Chem.* (in press).
10. R.P. Rapp, A. Mehta, J. DiCarlo, and A. Navrotsky. *J. Mater. Res.*, **9**, 8 (1994).
11. T.R.S. Prasanna and A. Navrotsky. *J. Mater. Res.* (submitted).