JOURNAL OF MATERIALS SCIENCE 23 (1988) 2735–2739

Estimation of oxygen pressures for the formation of superconducting phases based on La–Cu–O and Y–Cu–O systems

O. M. SREEDHARAN, C. MALLIKA, K. SWAMINATHAN
Materials Development Laboratory, Indira Gandhi Centre for Atomic Research, Kalpakkam 603 102, India

The use of thermodynamic data in the calculation of limiting oxygen pressures for the existence of ternary oxides is demonstrated in the case of $LaMO_3$ and La_2MO_4 (M = Mn, Fe, Co, Ni or Cu) compounds using the literature data on the relevant chemical equilibria. The standard Gibbs' energy of formation, ΔG_f^0, of $LaCuO_3$ is estimated from the values of ΔG_f^0 of the other $LaMO_3$ compounds calculated from the literature and is given as $(\Delta G^0_{f,LaCuO_3})$ (kJ mol^{-1}) = $-1095.0 + 0.2351\,T$ (K). The validity of this expression is qualitatively verified with the help of experimental conditions reported in the literature for the synthesis of this compound. Similar considerations are used to predict values of 0.03 and 30 atm to be the oxygen pressure range for the existence of a quarternary compound, $YBa_2Cu_3O_{9-y}$ at 1273 K. The superconducting transition temperature, T_c, is qualitatively predicted to show a maximum for the sample annealed under an oxygen pressure in the range 1 to 30 atm at 1273 K.

1. Introduction

Bednorz and Müller [1] reported superconductivity in $Ba_xLa_{5-x}Cu_5O_{5(3-y)}$ or $La_{1-x'}Ba_{x'}CuO_{3-y}$ (with x' = 0.2 and 0.15) with a superconducting transition temperature, T_c, of 30 K. Later, Politis *et al.* [2, 3] reported superconductivity in $La_{1.7}Ba_{0.3}CuO_{4-y}$, $La_{1.8}Sr_{0.2}CuO_{4-y}$ and in $Y_{1-x}Ba_xCuO_3$, which were synthesized by heating the binary oxide mixtures at temperatures above 1000 K in air. Similarly, $Y_{1.2}Ba_{0.8}CuO_{4-\delta}$ was found by Wu *et al.* [4] to have a value of T_c = 93 K: these authors annealed this compound in a reduced oxygen atmosphere at 1200 K. In general it appears that the synthesis of these superconducting mixed oxides is at present considered more an art than science, because of the lack of data on the dependence of superconductivity on the oxygen partial pressure under which these compounds were annealed at the temperature of the last step of their heat-treatment. It is well known that the oxygen stoichiometry of the condensed phase of a variable valency oxide is dictated by the oxygen partial pressure in the environment at the preparation temperature of the sample [5]. In addition, it is also known that the change in oxygen stoichiometry could be compensated by the change in the valency of the copper ion. According to Bednorz and Müller [1], the presence of Cu^{3+} (the formation of which is enhanced by divalent barium substitution of La^{3+}) could be responsible for the superconductivity of their compound, $La_{1-x'}Ba_{x'}CuO_{3-y}$. On the other hand, when all the copper was stabilized as trivalent Cu^{3+} ions, as in $LaSrCuO_4$, the compound was found to be a diamagnetic insulator exhibiting no superconductivity [6]. Hence the coexistence of Cu^{2+} and Cu^{3+} in such compounds appears to be a necessity [7] for superconducting behaviour. In the undoped La_2CuO_4, most of the copper would be present as Cu^{2+} ions. However, Cu^{3+} could be stabilized in a perovskite type of compound with the formula $LaCuO_3$ or $YCuO_3$ which is not stable in air at high temperatures. It should be pointed out that all the superconducting compounds referred to here are derived from $ACuO_3$ or A_2CuO_4 (where A is La or Y) by their solid solution with BaO or SrO and therefore an attempt is made in this paper to estimate the stability of $LaCuO_3$ in terms of the thermodynamic data available for other $LaMO_3$ phases (where M = Mn, Fe, Co or Ni) such that the limiting oxygen partial pressures could be derived for the coexistence of di- and trivalent copper ions. Besides the fact that such oxygen pressures estimates could help in the choice of atmospheric conditions for the synthesis of oxide superconductors, it would also serve as an indication as to how oxygen pressures could be derived from Gibbs' energy data for use by materials scientists. Such a treatment could also be extended to the oxides derived from $YCuO_3$.

2. Oxygen potential data on La–M–O systems (M = Mn, Fe, Co or Ni)

In the La–M–O systems, different phases coexist with the perovskite $LaMO_3$ phase for different M elements [8, 9]. For example, $LaMnO_3$ coexists with La_2O_3 and MnO whereas $LaFeO_3$ would coexist with La_2O_3 and Fe (but not "FeO" or Fe_3O_4) at temperatures in the vicinity of 1273 K. However, $LaCoO_3$ [8] and $LaNiO_3$ [9] coexist with La_2CoO_4/CoO and La_2NiO_4/NiO, respectively, under similar conditions. The reactions between these phase mixtures that fix the oxygen partial pressure by the phase rule, and the least-squares

0022–2461/88 $03.00 + .12

TABLE I Equilibrium oxygen pressures of the three solid phase mixtures in La–M–O systems (M = Mn, Fe, Co, Ni or Cu)

Equilibrium reactions	($\log P_{O_2}$) (atm) $= A - B/T$ (K)	Temperature range (K)	Reference
1. $2La_2O_3 + MnO + O_2(g) \rightleftharpoons 4\ LaMnO_3$	$13.58 - 35\,139/T$	1064–1308	[32, 33]
2. $\frac{2}{3}La_2O_3 + \frac{4}{3}Fe + O_2(g) \rightleftharpoons \frac{4}{3}LaFeO_3$	$5.81 - 28\,879/T$	1094–1299	[8]
3. $2La_2CoO_4 + 2CoO + O_2(g) \rightleftharpoons 4LaCoO_3$	$8.89 - 20\,476/T$	1212–1325	[10, 34]
4. $2La_2NiO_4 + 2NiO + O_2(g) \rightleftharpoons 4LaNiO_3$	-6.00*	1273	[9]
5. $2La_2O_3 + 2Co + O_2(g) \rightleftharpoons 2La_2CoO_4$	$6.10 - 23\,489/T$	973–1375	[10]
6. $2La_2O_3 + 2Ni + O_2(g) \rightleftharpoons 2La_2NiO_4$	$5.76 - 21\,804/T$	1123–1373	[10, 35]
7. $2La_2O_3 + 4LaCuO_2 + O_2(g) \rightleftharpoons 4La_2CuO_4$	$7.64 - 15\,545/T$	970–1370	[10, 11]
8. $4La_2O_3 + 2Cu_2O + O_2(g) \rightleftharpoons 4La_2CuO_4$†	$8.07 - 15\,459/T$	1220–1340	[12]
9. $2La_2O_3 + 4Cu + O_2(g) \rightleftharpoons 4LaCuO_2$	$8.02 - 18\,563/T$	1140–1260	[11]

*Nakamura *et al.* [9]; only measured at 1273 K.

†Not an equilibrium mixture but yields values of oxygen potential not too different from the mixture in Reaction 7 as pointed out by Chandrasekharaiah *et al.* [11].

expressions for the $\log P_{O_2}$ for the coexistence of these phases derived from solid electrolyte e.m.f. measurements, are listed in Table I. Also listed in this table are the corresponding data from the literature on the three-phase mixtures bearing the ternary oxide La_2MO_4. These are included here because the data on the stability of La_2MO_4 are required for evaluating that of $LaMO_3$ as in the case of nickel or cobalt. A relevant observation should be made here with respect to the two sets of phases reported in the literature [9–11] for the coexistence with La_2CuO_4. These mixtures were $La_2CuO_4/La_2O_3/LaCuO_2$ reported by Sreedharan and Pankajavalli [10] in contrast to $La_2CuO_4/La_2O_3/Cu_2O$ reported by Tretyakov *et al.* [12] (who ignored the formation of $LaCuO_2$ in a mixture of La_2O_3 and Cu_2O). However, the difference between these two sets of data would not be more than 6.0 kJ at 1273 K per gram atom of oxygen, which is not too large, but significant. The thermochemical equations making use of these oxygen potential data for the derivation of standard Gibbs' energy of formation, ΔG_f^0 of the relevant ternary compounds are given below.

3. Standard Gibbs' energy of formation of LaMO₃ (M = Mn, Fe, Co or Ni)

The oxygen potentials in the three-phase mixtures measured by e.m.f. technique (or by any other suitable method) could be readily related to the standard Gibbs' energy changes for the reactions occurring in them. For example, in the case of $LaMnO_3$, the reaction that fixed the oxygen potential ($RT \ln P_{O_2}$) at a constant temperature can be given as

$$\tfrac{1}{2}La_2O_3 + MnO + \tfrac{1}{4}O_2(g) \rightleftharpoons LaMnO_3 \qquad (1)$$

The standard Gibbs' energy change, ΔG_r^0, for Reaction 1 is related to the ΔG_f^0 of the reactants and products in their standard state by the simple equality

$$\Delta G_{r,1}^0 = \Delta G_{f,LaMnO_3}^0 - \tfrac{1}{2}\Delta G_{f,La_2O_3}^0 - \Delta G_{f,MnO}^0 \qquad (2)$$

When the condensed phases are assumed to be in their standard states, their thermodynamic activities, a, can be assumed to be unity. Hence the relation between $\Delta G_{r,1}^0$ and the equilibrium constant, K, with the equilibrium oxygen pressure, P_{O_2} can be simplified to

$$\Delta G_{r,1}^0 = -RT \ln K = \tfrac{1}{4}RT \ln P_{O_2(equ)} \qquad (3)$$

Using Equations 2 and 3 along with the Gibbs' energy data on MnO and La_2O_3 assessed in the literature [13–18], the ΔG_f^0 of $LaMnO_3$ was computed and is given in Table II. Similar data on the ΔG_f^0 of $LaFeO_3$ and $LaCoO_3$ were calculated from the $\log P_{O_2}$ expressions in Table I and from the Gibbs' energy data on the binary oxides from the literature [15–21] and are also listed in Table II. This exercise was carried out here because the ΔG_f^0 of $LaMO_3$ had not been computed from the $\log P_{O_2}$ data in the earlier works. In the case of $LaNiO_3$, Nakamura *et al.* [9] measured a value of -6.0 atm for the $\log P_{O_2}$ (Table I) of the mixture $LaNiO_3/La_2NiO_4/NiO$ at 1273 K from which a value of $-889.5\ \text{kJ mol}^{-1}$ (Table II) was derived for the ΔG_f^0 of $LaNiO_3$. As no reliable measurement is reported on $LaCuO_3$ in the literature, an attempt is made here to estimate the value of ΔG_f^0 by extrapolation. (The extrapolation of the standard Gibbs' energy data from e.m.f. measurements is generally more acceptable [19, 22] than the extrapolation of the enthalpy and entropy terms (the intercept and the slope) in the equation relating the Gibbs' energy with temperature.)

For this purpose, the values of ΔG_f^0 of these $LaMO_3$ compounds are plotted against the atomic number of the transition element, M, as shown in Fig. 1. From a least-squares fitting of the points in this figure a value of $-794.9\ \text{kJ mol}^{-1}$ could be assessed for the formation of the $LaCuO_3$ phase. To compute the dissociation pressure of this compound, it is necessary to consider the following reaction between the phases which are those most likely to coexist at 1273 K:

$$\tfrac{1}{2}La_2CuO_4 + \tfrac{1}{2}CuO + \tfrac{1}{4}O_2(g) \rightleftharpoons LaCuO_3 \qquad (4)$$

Combining Equation 4 with the ΔG_f^0 data from Table II, a value of $57.4\ \text{kJ mol}^{-1}$ could be estimated for the oxygen potential ($RT \ln P_{O_2}$) for Reaction 4 at 1273 K. Thus the standard Gibbs' energy change, ΔG_r^0, for Reaction 4 (which is equal to $\frac{1}{4}RT \ln P_{O_2}$) is calculated only at a temperature of 1273 K because of the lack of $LaNiO_3$ data [9] at any other temperature, for observing a systematic trend as in Fig. 1.

In the absence of any other information, a temperature dependent expression for the $\Delta G_{r,4}^0$ could be given only from an estimate of the entropy change for this reaction, ignoring the contribution of the condensed phases to the entropy change. Thus the entropy change, $\Delta S_{r,4}^0$, could be taken to be approximately $-20\ \text{J K}^{-1}\ \text{mol}^{-1}$ corresponding to one-fourth of the molar translational entropy of oxygen gas.

TABLE II Standard Gibbs' energies of formation of $LaMO_3$ and La_2MO_4 computed from experimental data*

Compound	ΔG_f^0 (kJ mol^{-1}) $= -A + BT$ (K)	$\Delta G_{f,1273\,K}^0$ (kJ mol^{-1})	Reference for $\Delta G_{f,MO}^0$†
1. $LaMnO_3$	$-1484.2 + 0.2778\,T$	-1130.5	[13–17]
2. $LaFeO_3$	$-1341.6 + 0.2196\,T$	-1062.0	[21]
3. $LaCoO_3$	$-1258.5 + 0.2493\,T$	-941.2	[10, 15, 19, 20]
4. $LaNiO_3$	-889.5‡	-889.5	[15, 36]
5. $LaCuO_3$	$-1095.0 + 0.2351\,T$	-795.7	[15, 23]
6. La_2CoO_4	$-2075.2 + 0.3281\,T$	-1657.6	[10, 19, 20]
7. La_2NiO_4	$-2062.6 + 0.3275\,T$	-1645.7	[15, 36]
8. La_2CuO_4§	$-2017.2 + 0.3474\,T$	-1575.0	[15, 23]
9. $LaCuO_2$	$-1019.9 + 0.1785\,T$	-792.7	[11, 15]

*Computed using the data from (a) Table I, (b) $\Delta G_{f,La_2O_3}^0$ given by Kubaschewski and Alcock [18], and (c) the references in the last column.

†References to both the original data and critical assessments are given.

‡Calculated only at 1273 K.

§Calculated based on the data in Reaction 7 of Table I.

Thus

$$(\Delta G_{r,4}^0)\ (\text{kJ mol}^{-1}) = -11.10 + 0.02\,T\ (\text{K}) \qquad (5)$$

Equation 5 is combined with the ΔG_f^0 of La_2CuO_4 from Table II and the ΔG_f^0 of CuO from the literature [15, 16, 23] to yield the following expression for the formation of $LaCuO_3$ from its elements in their standard states:

$$(\Delta G_{f,LaCuO_3}^0)\ (\text{kJ mol}^{-1}) = -1095.0 + 0.2350\,T\ (\text{K}) \qquad (6)$$

To assess the reliability of Equation 5 it is converted into an expression for the limiting oxygen pressure for the dissociation of $LaCuO_3$ in accordance with Reaction 4 as given below.

$$(\log P_{O_2})\ (\text{atm}) = 4.18 - 2319.4/T\ (\text{K}) \qquad (7)$$

Equation 7 gives values of 104 and 228 atm for the limiting oxygen pressure for Reaction 4 at 1073 and 1273 K, respectively. These are of the same order of magnitude as 400 atm at 1073 K employed for the synthesis of $LaCuO_3$ by Arjomand and Machin [24]. These values are, however, lower than 65×10^3 atm pressure employed by Demazeau *et al.* [25] for the synthesis of $LaCuO_3$ in a bath of $KClO_3$ at 1173 K. Such large pressures used by the latter workers were, perhaps, required for the purpose of achieving appreciable solubility of the oxides in $KClO_3$, but their method of synthesis confirms the coexistence of the condensed phases given by Reaction 4.

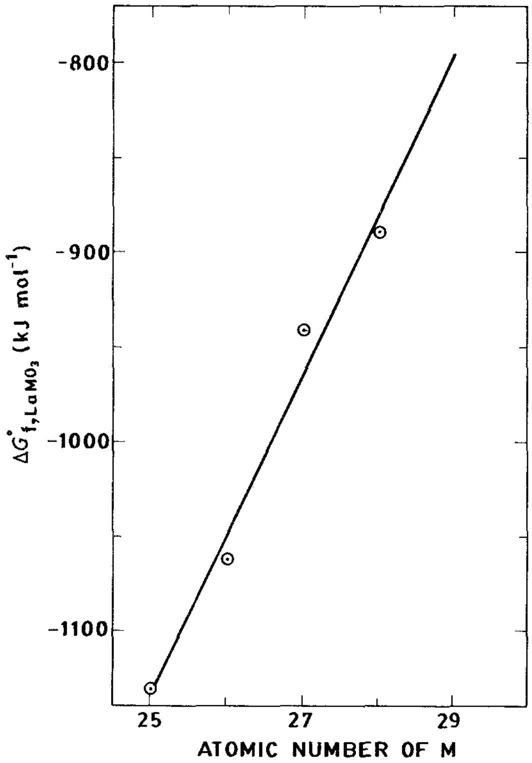

Figure 1 Systematic trend in the ΔG_f^0 of $LaMO_3$ for some first-row transition metals.

4. Limiting oxygen pressures for the dissociation of $LaMO_3$ and La_2MO_4

The limiting oxygen pressure below which $LaCuO_3$ would dissociate in accordance with Equation 4 is thus found to be 228 atm at 1273 K. The corresponding values for the limiting oxygen pressures for $LaCoO_3$ and $LaNiO_3$ undergoing reactions identical to Reaction 4 were also computed at 1273 K and are given in Table III for the purpose of comparison. These limiting pressure values are uniquely fixed by the phase rule. The oxygen pressures below which La_2MO_4 would dissociate are also given in this table. In the case of manganese and iron, compounds of the formula La_2MO_4 are not thermodynamically stable [10] and therefore only the corresponding dissociation pressures of $LaMO_3$ are included here.

From Table III one can infer the range of log P_{O_2} between the dissociation equilibria of La_2CuO_4 and $LaCuO_3$ to be -4.57 and 2.37 atm at 1273 K which would serve as a rough indication of the oxygen pressure limits for the coexistence of Cu^{2+} and Cu^{3+} in a quarternary compound containing strontium or barium. Before further discussion on the lanthanum-bearing quaternary oxides, it would be worthwhile to

TABLE III Limiting oxygen pressures for the dissociation of $LaMO_3$ and La_2MO_4 at 1273 K

M	($\log P_{O_2}$) (atm) for the dissociation of	
	$LaMO_3$	La_2MO_4
Mn	-14.02	*
Fe	-16.88	*
Co	-7.20	-12.35
Ni	-6.00	-11.37
Cu	2.37†	-4.57

*Not formed.

†Calculated from $\Delta G_{f,LaCuO_3}^0$ estimated from Fig. 1 by extrapolation.

consider the limiting pressures for the dissociation of $YCuO_3$. In the Y–Cu–O system, above 1000 K only the compounds $Y_2Cu_2O_5$ ($YCuO_{2.5}$) and $YCuO_3$ appear to be relevant to the present discussion, because Y_2CuO_4 had not been reported in the literature. The dissociation equilibria involving these oxides could be represented as

$$YCuO_{2.5} + \tfrac{1}{4}O_2(g) \rightleftharpoons YCuO_3 \qquad (8)$$

The dissociation pressure of Reaction 8 has not been reported so far. Arjomand and Machin [24] had synthesized $YCuO_3$ from a mixture of Y_2O_3 and CuO by heating them at 1073 K under an oxygen pressure of 400 atm (similar to the synthesis of $LaCuO_3$). Therefore, one can take the limiting pressure for the dissociation of $YCuO_3$ to be of the same order as that for $LaCuO_3$, i.e. a value of +2 atm for $\log P_{O_2}$ at 1273 K can be taken as a reasonable estimate. For the reaction

$$\tfrac{1}{2}Y_2O_3 + \tfrac{1}{2}Cu_2O + \tfrac{1}{4}O_2(g) \rightleftharpoons YCuO_{2.5} \qquad (9)$$

the oxygen potential was reported by Tretyakov *et al.* [12] over the range 1173 to 1340 K from e.m.f. measurements. From their data the following expression for $\log P_{O_2}$ could be derived.

$$(\log P_{O_2})\ (\mathrm{atm}) = 7.83 - 11910/T\ (\mathrm{K}) \qquad (10)$$

Thus it can be seen that the limiting values of $\log P_{O_2}$ for the dissociation of $Y_2Cu_2O_5$ and $YCuO_3$ at 1273 K are taken as −1.53 and +2 atm, respectively. Just as in the case of the La–Cu–O system, these values give the range of $\log P_{O_2}$ within which Cu^{2+} and Cu^{3+} could coexist in a quarternary compound based on Y–Cu–O containing strontium or barium.

5. Application of limiting oxygen pressures for the synthesis of quarternary superconducting oxides

An examination of the compositions of mixed oxide superconductors reported in the literature [1–4, 26–30] shows that only a very small fraction of lanthanum could be replaced by strontium or barium in La_2CuO_4 or $LaCuO_3$, whereas a much larger fraction of yttrium could be replaced by Ba^{2+} in $YCuO_3$, for example in $Y_{0.33}Ba_{0.67}CuO_{3-y}$ reported by Cava *et al.* [29]. If one applies the $\Delta G^0_{r,8}$ in the case of barium substituted $YCuO_3$, then

$$\Delta G^0_{r,8} = -RT \ln a_{YCuO_3}/a_{YCuO_{2.5}}P_{O_2}^{1/4} \qquad (11)$$

where a is the activity of the pure ternary oxides in the quarternary compound. In the case of barium dissolving exclusively in the $YCuO_3$ phase but very little in the $YCuO_{2.5}$ phase, at the threshold of precipitation of the $YCuO_{2.5}$ phase the value of a_{YCuO_3} and $a_{YCuO_{2.5}}$ could be roughly taken to be 0.33 and 1, respectively, in the absence of any other information. This leads to a value of > 30 atm for P_{O_2} to fix all copper in the +3 state based on a value of 10^2 assumed for the P_{O_2} (equilibrium) for Reaction 8 at 1273 K. A sample of average composition $Y_{0.2}Ba_{0.8}CuO_{3-y}$ was prepared in our laboratory by heating the oxide mixtures either in air or in oxygen at 1173 K. Superconductivity measurements carried out by Radhakrishnan *et al.* [31] on these samples showed a value of T_c = 35 K for the air-heated sample and a value of 85 K for the oxygen heated sample. Because the limiting pressures discussed earlier show the P_{O_2} range to be 0.03 to 100 atm, it can be inferred that a maximum T_c might occur somewhere between 1 and 30 atm. Direct thermodynamic measurements of the oxygen potentials based on the well-established phase relationships in the La–Ba–Cu–O and Y–Ba–Cu–O systems are necessary for any further prediction of the optimum values of temperature and oxygen pressure for the synthesis of superconducting oxides.

Acknowledgements

The authors thank Shri C. V. Sundaram, Director, IGCAR, Dr P. Rodriguez, Head, Metallurgy Programme and Shri J. B. Gnanamoorthy, Head, Chemical Metallurgy Section, Materials Development Laboratory for their keen interest and constant encouragement throughout the course of this work. They also wish to thank Drs T. S. Radhakrishnan, U. De and J. Janaki, Materials Science Laboratory, IGCAR for useful discussions.

References

1. J. G. BEDNORZ and K. A. MÜLLER, *Z. Phys.* **B64** (1986) 189.
2. C. POLITIS, J. GEERK, M. DIETRICH and B. OBST, *ibid.* **B66** (1987) 141.
3. C. POLITIS, J. GEERK, M. DIETRICH, B. OBST and H. L. LUO, *ibid.* **B66** (1987) 279.
4. M. K. WU, J. R. ASHBURN, C. J. TORNG, P. H. HOR, R. L. MENG, L. GAO, Z. J. HUANG, Y. Q. WANG and C. W. CHU, *Phys. Rev. Lett.* **58** (1987) 908.
5. H. G. SOCKEL and H. SCHMALZRIED, *Ber. Bunsenges. Phys. Chem.* **72** (1968) 745.
6. C. N. R. RAO and P. GANGULY, *Curr. Sci.* **56** (1987) 47.
7. R. JAGADISH and K. P. SINHA, *ibid.* **56** (1987) 291.
8. O. M. SREEDHARAN and M. S. CHANDRASEKHARAIAH, *J. Mater. Sci.* **21** (1986) 2581.
9. T. NAKAMURA, G. PETZOW and L. J. GAUCKLER, *Mater. Res. Bull.* **14** (1979) 649.
10. O. M. SREEDHARAN and R. PANKAJAVALLI, *J. Mater. Sci. Lett.* **3** (1984) 388.
11. M. S. CHANDRASEKHARAIAH, M. D. KARKHANAVALA and O. M. SREEDHARAN,*High Temp. Sci.* **11** (1979) 65.
12. YU. D. TRETYAKOV, A. R. KAUL and N. V. MAKUKHIN, *J. Solid State Chem.* **17** (1976) 183.
13. C. B. ALCOCK and S. ZADOR, *Electrochim. Acta* **12** (1967) 673.
14. A. V. RAMANA RAO and V. B. TARE, *Trans. Inst. Min. Met.* **82** (1973) C34.
15. O. M. SREEDHARAN and C. MALLIKA, "A Compilation of Gibbs' Energy Data for 40 Metal Oxide Buffers", Report No. RRC-69 (Reactor Research Centre, Kalpakkam, 1984) p. 21.
16. L. B. PANKRATZ, J. M. STUVE and N. A. GOKCEN, "Thermodynamic Data for Mineral Technology" (Bureau of Mines Bulletin 677, Washington, 1984) pp. 261-95.
17. O. M. SREEDHARAN, PhD thesis, University of Bombay, India (1975).
18. O. KUBASCHEWSKI and C. B. ALCOCK, "Metallurgical Thermochemistry", 5th Edn (Pergamon, Oxford, 1983) p. 381.
19. O. M. SREEDHARAN, M. S. CHANDRASEKHARAIAH and M. D. KARKHANAVALA, *High Temp. Sci.* **9** (1977) 109.
20. O. M. SREEDHARAN and C. MALLIKA, *Mater. Chem.*

Phys. **14** (1986) 375.
21. R. A. GIDDINGS and R. S. GORDON, *J. Amer. Ceram. Soc.* **56** (1973) 111.
22. O. KUBASCHEWSKI, *High Temp. High Press.* **4** (1972) 1.
23. G. G. CHARATTE and S. N. FLENGAS, *J. Electrochem. Soc.* **115** (1968) 796.
24. M. ARJOMAND and D. J. MACHIN, *J. Chem. Soc. Dalton* (1975) 1061.
25. G. DEMAZEAU, C. PARENT, M. POUCHARD and P. HAGENMULLER, *Mater. Res. Bull.* **7** (1972) 913.
26. C. W. CHU, P. H. HOR, R. L. MENG, L. GAO, Z. J. HUANG and Y. Q. WANG, *Phys. Rev. Lett.* **58** (1987) 405.
27. C. W. CHU, P. H. HOR, R. L. MENG, L. GAO and Z. J. HUANG, *Science* **235** (1987) 567.
28. R. J. CAVA, R. B. VAN DOVER, B. BATLOGG and E. A. RIETMAN, *Phys. Rev. Lett.* **58** (1987) 408.
29. R. J. CAVA, B. BATLOGG, R. B. VAN DOVER, D. W. MURPHY, S. SUNSHINE, T. SIEGRIST, J. P. REMEIKA, E. A. RIETMAN, S. ZAHURAK and G. P. ESPINOSA, *ibid.* **58** (1987) 1676.
30. I. K. GOPALAKRISHNAN, A. M. UMARJI, J. V. YAKHMI, L. C. GUPTA, R. M. IYER and R. VIJAYARAGHAVAN, *Mater. Lett.* **5** (1987) 165.
31. T. S. RADHAKRISHNAN, U. DE and J. JANAKI, Materials Science Laboratory, Indira Gandhi Centre for Atomic Research, Kalpakkam (personal communication).
32. O. M. SREEDHARAN, R. PANKAJAVALLI and J. B. GNANAMOORTHY, *High Temp. Sci.* **16** (1983) 251.
33. O. M. SREEDHARAN, R. PANKAJAVALLI and J. B. GNANAMOORTHY, *Mater. Lett.* **2** (1984) 547.
34. O. M. SREEDHARAN and M. S. CHANDRASEKHARAIAH, *Mater. Res. Bull.* **7** (1972) 1135.
35. O. M. SREEDHARAN, M. S. CHANDRASEKHARAIAH and M. D. KARKHANAVALA, *High Temp. Sci.* **8** (1976) 179.
36. H. H. KELLOGG, *J. Chem. Eng. Data* **14** (1969) 41.

Received 3 August
and accepted 22 October 1987