

Carbonatization of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$

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$\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ reacts with CO_2 at a significant rate at temperatures above $\sim 400^\circ\text{C}$. The stability of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ towards reaction with CO_2 in $\text{CO}_2 + \text{O}_2$ mixtures ($p_{\text{O}_2} \approx 1.00 \text{ atm}$) has been established as a function of CO_2 partial pressure and temperature. Below $730 \pm 10^\circ\text{C}$ the reaction products are BaCO_3 , Y_2O_3 and CuO . Above this temperature the products are BaCO_3 , $\text{Y}_2\text{Cu}_2\text{O}_5$ and CuO . Thermodynamic parameters for the two reactions have been evaluated for $x = 0.5$.

The recently discovered class of high T_C superconducting oxides has properties which open up for many applications. The first efforts to explore the properties of these compounds were naturally concentrated on the characterization of phase diagrams and crystal structures, as well as on the systematic mapping of key physical parameters. However, in order to evaluate their potential use in practical superconducting devices, properties connected with grain boundaries, surfaces and, in particular, chemical reactivity towards environmental components become of utmost importance.

The superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{9-\delta}$ phase (in the following most conveniently expressed as $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ with $0 \leq x \leq 1$) is reported to be degraded by water.¹⁻³ Upon heating or when exposed to lower partial pressures of oxygen, the oxygen content is reduced from a maximum of seven to a minimum of six atoms per formula unit.⁴⁻⁹ Reactions with gaseous species during the syntheses may be important and it has, for instance, been reported¹⁰ that in interaction with N_2 at elevated temperature some nitrogen can replace oxygen in $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$. Unfortunately, many studies on the new oxide superconductors have been performed on phase-impure samples. The latter problem derives partly from a lack of knowledge of the phase diagram and inappropriate preparative procedures.

The metal constituents of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ exhibit a relatively high average electropositive character, and the interdependent high basicity¹¹ of the

constituent oxides (in particular BaO) suggests that a detectable reaction between the quaternary oxide and CO_2 could proceed even at relatively low CO_2 partial pressures and high temperatures. In order to make practical use of the superconducting phases it is important to clarify this aspect.

The p, T equilibrium for decomposition of carbonates can be established using static¹² or dynamic¹³ methods. The former procedure is based on *direct measurements* of the CO_2 decomposition pressure at fixed temperatures. In the dynamic procedure, on the other hand, one of the thermodynamic variables (e.g. T) is set at a value around the expected equilibrium value and the *response of the reaction system* is registered while monitoring the second variable (e.g. p_{CO_2}).

The present paper reports on dynamic thermogravimetric measurements made under conditions of varying temperature and CO_2 partial pressure. The apparatus and procedures employed are similar to those in the cyclic thermogravimetric method reported recently.¹⁴ The method has the great advantage of being sensitive to even small degrees of carbonatization of the oxide samples.

Materials and methods

Preparation. The quaternary oxide was prepared from CuO , BaCO_3 (both reagent grade; Merck) and Y_2O_3 (99.999%; Megon, Norway). A stoichiometric mixture of the dried and analyzed

components was homogenized to a slurry by milling under acetone in a Fritsch Pulverisette laboratory grinder for 12 h. After firing at 900 °C in air for 24 h, the product was re-homogenized twice by milling under carbon tetrachloride and re-annealed under similar conditions in the form of sieved powder in a corundum boat. The final sequence comprised a 24 h annealing in air at 400 °C.

Chemical analysis. The copper and oxygen contents were determined iodometrically using 0.1 M $\text{Na}_2\text{S}_2\text{O}_3$ (Titrisol; Merck) standardized against KIO_3 . Approximately 0.2 g of an accurately weighed, pulverized sample was dissolved in 1 M HCl in an Erlenmeyer flask, the solution heated to dryness and the residue redissolved in acidified water. The iodine released after adding ~1 g of KI in 20 ml of water was titrated, thus providing a measure of the copper content. The total oxidative power towards I^- was determined separately. The iodine (to be titrated) was then released during reaction of a suspension of the (previously weighed) sample in 20 ml of 5% KI to which 10 ml of 1 M HCl was slowly added during stirring (the Erlenmeyer flask being filled with argon in advance). No analyses for yttrium or barium were performed since all samples used in this study were shown by X-ray diffraction to be single-phase; this fixes the contents of these elements relative to copper according to the stoichiometry of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$.

X-Ray diffraction. The homogeneity of all samples was checked at room temperature by powder X-ray diffraction using a Guinier Hägg camera ($\text{CuK}\alpha_1$ and $\text{CrK}\alpha_1$ radiation, Si as internal standard). Corresponding high-temperature data were obtained between 20 and 1000 °C in a Guinier Simon camera. Unit cell dimensions were derived by least-squares refinements.¹⁵

Thermogravimetric measurements. The sample material was pulverized, and ~1.4 g of powder was weighed into a pre-annealed alumina crucible.

A Sartorius model 4410 balance was used, with platinum wires suspended on both balance arms. One wire held the sample crucible inside a mullite tube in the hot zone of a tube furnace. The other wire held an identical counter-weight crucible inside a glass tube at room temperature. The

tubes and the balance were part of a gas-tight system through which gas mixtures could be fed.

The precision of the balance itself is 1 μg , but the use of elevated temperatures and gas flow past the sample introduced fluctuations that reduced the precision to about 10 μg . The long-term reproducibility was 40 μg .

The temperature was controlled and monitored by a Pt/Pt + 10% Rh thermocouple located close to the sample crucible. The thermocouple reading was checked against the true temperature in the crucible as follows: CaCO_3 (*p.a.*) powder was used as sample in ~1.00 atm of CO_2 . On increasing the temperature the weight of the sample started to decrease at 898 °C. On decreasing the temperature the weight increased at 897 °C. Thus, the apparent decomposition temperature of CaCO_3 under ~1.00 atm of CO_2 was assumed to be 897–898 °C. The decomposition of CaCO_3 has recently been carefully examined by a similar method, and a decomposition temperature of 897 °C at 1.00 atm of CO_2 was found.¹⁴ These results confirm that the thermocouple readings corresponded within ± 1 °C to the actual temperature at the crucible position.

Control of atmosphere. Controlled partial pressures of CO_2 were obtained by mixing CO_2 or air with oxygen in ratios of between 1 and 5000 using precision flowmeters. In this series of experiments the oxygen partial pressure was kept constant (~1.00 atm). The CO_2 content in the compressed air cylinders was reported to be 300 ppm. The oxygen used contained typically 14 ppm of CH_4 (which is assumed to react to give CO_2 in the furnace), and the CO_2 content in O_2 is therefore estimated to be 14 ppm. CO_2 contents above 200 ppm were produced by mixing CO_2 with O_2 . CO_2 contents between 14 and 100 ppm were obtained by mixing air with O_2 .

Atmospheres with variable O_2 partial pressures were established in the same system by mixing oxygen with argon.

The gas mixtures were dried with P_2O_5 . The total pressure in the furnace was around 1.00 atm, the exact value being monitored with a manometric pressure gauge.

Thermogravimetric procedures. The stability of the quaternary oxide with regard to carbonate formation was studied as follows: At each partial pressure of CO_2 the temperature was increased

or decreased in steps, and the change in the sample weight was recorded. A weight increase is assumed to correspond to carbonate formation, and a weight decrease to carbonate decomposition (i.e. the quaternary oxide is stable). The equilibrium was found by averaging the two closest points representing weight increase and decrease, or as points where no weight change could be observed. The determination of the equilibrium temperature was performed with a precision ranging from about 1 °C above 800 °C to about 10 °C below 700 °C.

When significant amounts of CO₂ or air were added to the oxygen, minor weight changes occurred due to the corresponding changes in the oxygen partial pressure. These changes could, however, be distinguished from those associated with the carbonate reaction by their different kinetic behaviour: The reaction with O₂ is fast and the sample weight rapidly reaches a new equilibrium value, while the CO₂ reaction is slow and the sample weight continues to change for extended periods.

The determination of the changes in oxygen content of the sample for each set of temperature and oxygen partial pressure conditions was done using standard thermobalance calculations based on relative weight readings and on the weight and oxygen content of the initial sample. Corrections were made for the buoyancy of both crucibles (with contents), taking into account temperature, composition of the gas mixture and total pressure. Loss of H₂O and CO₂ recorded during the very first heating cycle was used to correct the initial weight of the sample and the initial thermobalance weight reading.

Results and discussion

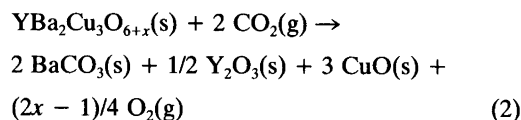
(i) *Structural properties.* Powder X-ray diffraction analysis confirmed that the YBa₂Cu₃O_{6+x} sample used in this study was single-phase with unit cell dimensions $a = 382.04 \pm 0.03$, $b = 388.82 \pm 0.03$ and $c = 1168.47 \pm 0.1$ pm. From iodometric titration the oxygen content was established to be 6.93 ± 0.02 per formula unit. The unit cell dimensions and particularly the degree of orthorhombic deformation agree with recently established⁶ correlations between structural characteristics and oxygen content.

Within the orthorhombic YBa₂Cu₃O_{6+x}-type variant of the perovskite atomic arrangement,

the easily removable oxygen atoms are (at low temperature) confined to one particular crystallographic site, viz. 0,1/2,0.¹⁶⁻¹⁹ High temperature powder X-ray diffraction studies (Guinier Simon technique) in air showed vanishing orthorhombic distortion at 690 ± 20 °C.²⁰ The "driving force" of the orthorhombic to tetragonal "phase transition" is redistribution of oxygen atoms over more sites – a process which takes place parallel with removal of oxygen from the structure. *Formally*, the redox process can be described as



(ii) *High-temperature reaction with CO₂.* Carbonatization of YBa₂Cu₃O_{6+x}, i.e. reaction with CO₂ to form carbonates, proceeds with measurable rates at temperatures above 400 °C. However, different reaction products are formed depending on the temperature. Below 730 ± 10 °C the oxides of yttrium and copper are formed together with barium carbonate:



Above 730 ± 10 °C, the turquoise blue Y₂Cu₂O₅ is a reaction product:

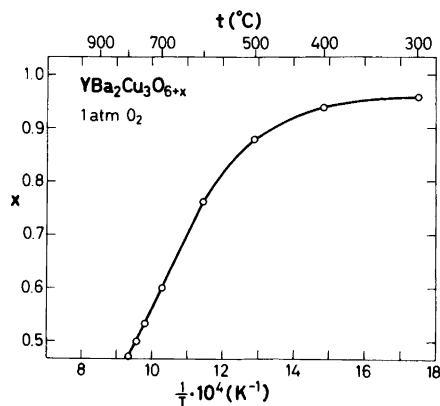
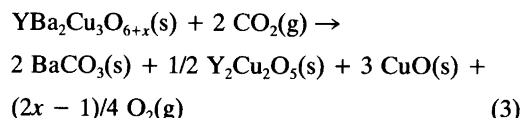


Fig. 1. Temperature dependence of oxygen content (x) of YBa₂Cu₃O_{6+x} at 1.00 atm of O₂.

The reactions proceed for certain combinations of the variables of x , p_{CO_2} , and T [see section (iv)]. In order to characterize the different reaction products, prolonged reaction times at 600 and 850 °C, respectively, followed by rapid cooling of the sample in the reaction atmosphere were adopted. The various phases were identified on the basis of powder X-ray diffraction diagrams, and the evaluated unit cell dimensions corresponded well with those found for the pure products.²⁰ Thus, mutual solid solubility of the reaction products was negligible.

(iii) *High temperature reaction with O_2 in mixture with CO_2 .* Some investigators have claimed that $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ is able to accommodate nitrogen in oxygen sites.¹⁰ The present thermogravimetric measurements in O_2/Ar and O_2/N_2 (20/80 v/v) mixtures at 600 °C gave no support for such a conclusion.

The oxygen content of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ is a function of both temperature and oxygen partial pressure. For $x = 0.50$ the oxidation state of copper is equal in the reactants and the products, and no oxygen is evolved or consumed during the carbonatization [eqns. (2) and (3)]. However, in general the carbonatization involves either release ($x > 0.5$) or uptake ($x < 0.5$) of oxygen. Thus, a quantitative treatment of the reactions with CO_2 will require knowledge of the equilibrium between $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ and oxygen.

(iv) *x, p, T equilibrium in O_2 .* The oxygen content or the non-stoichiometry of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ varies

strongly with temperature, as illustrated in Fig. 1 for a constant oxygen partial pressure of 1.00 atm. Under such conditions the maximum oxygen content corresponds to $x = 0.955$, which is in agreement with earlier reported equilibrium data.^{1,8} The x versus $1/T$ relationship is essentially linear in the temperature range 600–900 °C, and can be parameterized as:

$$x = A/T + B \quad (4)$$

where A and B have values of 1390 K and -0.83 , respectively.

The oxygen partial pressure in equilibrium with $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$ is plotted versus reciprocal temperature in Fig. 2 for the temperature interval 520–780 °C. The relationship can empirically be described as:

$$\log p_{\text{O}_2} = C/T + D \quad (5)$$

with $C = -8350$ K and $D = 8.0$ for p_{O_2} specified in atm. According to Fig. 2, $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$ is stable at ~ 775 °C in pure oxygen (1.00 atm) and at ~ 690 °C in air. These temperatures coincide with those for the orthorhombic to tetragonal structural transition. Independent studies^{21–24} have found the latter structural transition to occur for $x = 0.5$ in different atmospheres. The p_{O_2} versus

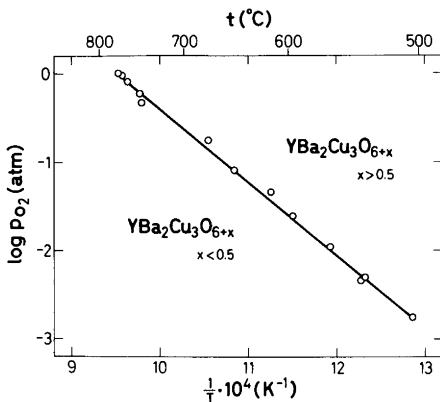


Fig. 2. Partial pressure of oxygen in equilibrium with $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$ as a function of temperature.

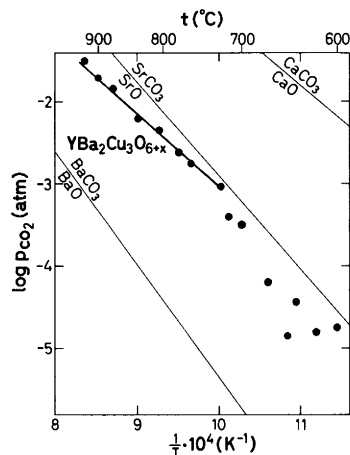


Fig. 3. Stability of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ with respect to carbonate formation ($p_{\text{O}_2} \approx 1.00$ atm). The equilibrium state is tentatively indicated by the solid line and shaded strip. Thinner lines depict data for alkaline earth carbonates/oxides for comparison.

$1/T$ relationship for $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$ also corresponds, to a good approximation, to the variation of the distortion temperature with the oxygen pressure.

(v) *p,T equilibrium for reaction with CO_2* . The results of the reaction studies on $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ in CO_2 -containing atmospheres are summarized in the $\log p_{\text{CO}_2}$ versus $1/T$ plot in Fig. 3. The fully-drawn line and the shaded strip in Fig. 3 separate the stability regions of reactants and products. The quaternary oxide is thus stable at higher T and lower p_{CO_2} . Consistent with the observation of two different sets of reaction products, the equilibrium boundary shows a kink or jump at around 730°C.

At lower temperature and reduced p_{CO_2} , any weight changes become increasingly difficult to register. This is probably due to slower diffusion of carbon dioxide and/or metal atoms in the sample, and to the low CO_2 content of the atmosphere itself. The measurements at the lowest CO_2 partial pressures are furthermore burdened by the rather uncertain estimate of the content of carbonaceous impurities in the oxygen gas. Additional sources of uncertainty concerning these conditions may originate from competing reactions with the inevitable trace amounts of H_2O present in the gas mixtures, and the fact that formation of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ from the oxide constituents is slow at the temperatures concerned. Thus, while the equilibrium line for reaction according to eqn. (3) can be well established, the equilibrium for eqn. (2) cannot be determined with the same accuracy.

At 300°C in air no carbonatization could be detected (although thermodynamically it should take place, Fig. 3), at 400°C the reaction proceeds at a rate of $\sim 0.006\%$ per hour, while at 500 and 600°C the corresponding rates amount to 0.026 and 0.047% per hour, respectively. The reaction rate at 600°C may be limited by the rate of supply of CO_2 .

The equilibrium diagram in Fig. 3 puts restrictions on the procedures for the synthesis of high-purity $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$. The compound can only be successfully prepared from BaCO_3 and oxides under conditions to the left of the equilibrium boundary in Fig. 3. The CO_2 content of air (300 ppm) and the content of carbonaceous gases in commercial, pressurized oxygen (~ 10 ppm) restrict the lowest temperatures for preparation

to 700 and 650°C, respectively. If crucibles with poor circulation of air/oxygen near the sample are used, it may be difficult to obtain a carbonate-free product even at significantly higher temperatures.

The superconductivity of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ is highly dependent on x , and the highest T_C is obtained for $x \approx 1.0$. Therefore, after the firing at some 900°C the samples are generally annealed at 300–400°C in air or oxygen in order to ensure a high oxygen content. The present results show that such a treatment may lead to partial carbonatization of the sample, impurities probably accumulating at grain boundaries and surfaces. This problem can be avoided by using CO_2 -free gases. Moreover, the annealing can be carried out at 250–300°C. At these temperatures the equilibration with respect to oxygen is reasonably fast, whereas the rate of carbonization is practically zero.

Included in Fig. 3 are the equilibria between oxides and carbonates of calcium, strontium and barium.^{25,26} It is seen that the properties of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ are comparable to those of SrO .

(vi) *Thermodynamic considerations*. The equilibrium data (Fig. 3) for the carbonatization reactions [eqns. (2) and (3)] can be expressed as standard enthalpy and entropy changes. However, the equilibrium CO_2 partial pressure refers to the $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ phase where x varies with temperature at constant $p_{\text{O}_2} = 1.00$ atm. Thus, the $\log p_{\text{CO}_2}$ versus $1/T$ relationship will, in principle, not be defined by a straight line. It is hence inconvenient for our purposes to define the reference state of the quaternary oxide as the stable composition at a given temperature and at $p_{\text{O}_2} = 1.00$ atm. Therefore, all calculations refer to the composition $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$, thus eliminating the internal redox reaction [eqn. (1)].

In the experiments, p_{O_2} was kept close to 1.00 atm, and in the temperature range in question, i.e. 650–930°C, the compositional variable x is fairly close to 0.5. This implies that the equilibrium expression for the chemical reactions [eqns. (2) and (3)] can be simplified according to:

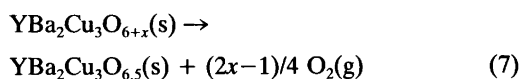
$$K_p = p_{\text{O}_2}^{(2x-1)/4} \cdot p_{\text{CO}_2}^{-2} \approx p_{\text{CO}_2}^{-2}. \quad (6)$$

In order to refer changes in the standard Gibbs energy, ΔG° , enthalpy, ΔH° , and entropy, ΔS° , to the reference composition $x = 0.5$, corrections due to the internal oxygen equilibrium reaction:

Table 1. Standard enthalpy and entropy changes for carbonatization of $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$.

Reaction No.	Temperature range/°C	$\Delta H^\circ/\text{kJ mol}^{-1}$	$\Delta S^\circ/\text{J mol}^{-1} \text{K}^{-1}$
(2) ^a	650–730	-680 ± 270	-570 ± 280
(3)	730–930	-346 ± 15	-229 ± 14

^aSee comments about uncertainty in section (v).



must be made. Thus, the change in standard Gibbs energy for the reactions (2) and (3) with $x = 0.5$ is:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 2RT \cdot \ln p_{\text{CO}_2} - \Delta G_{\text{redox}}^\circ \quad (8)$$

where

$$\Delta G_{\text{redox}}^\circ = (1-2x)/4 \cdot RT \cdot \ln p_{\text{O}_2} \quad (9)$$

On introduction of the empirically deduced relations, eqns. (4) and (5) for the temperature dependences of x and $\log p_{\text{O}_2}$, $\Delta G_{\text{redox}}^\circ$ for the chemical reaction (7) becomes:

$$\Delta G_{\text{redox}}^\circ = \alpha T + \beta + \gamma/T \quad (10)$$

where $\alpha = 0.102 \text{ kJ K}^{-1} \text{ mol}^{-1}$, $\beta = -212.7 \text{ kJ mol}^{-1}$ and $\gamma = 111.2 \cdot 10^3 \text{ kJ K mol}^{-1}$ over the temperature range 600–900°C. The derived values of ΔH° and ΔS° for the reactions in eqns. (2) and (3) with $x = 0.5$ are given in Table 1. On the basis of the thermodynamic data for the reaction components [eqn. (2); assuming $\Delta C_p = 0$ for the reaction] listed in the JANAF tables,²⁷ the standard enthalpy of formation for $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$ is $\Delta H_{f,298}^\circ = -2400 \pm 270 \text{ kJ mol}^{-1}$ (no data are available for $\text{Y}_2\text{Cu}_2\text{O}_5$).

On comparing the deduced ΔG° values for the oxygen shift reaction [eqn. (7)] and the carbonatization reactions [eqns. (2) and (3)] at various temperatures, it is seen that ΔG° for the former reaction is comparable in magnitude with the uncertainty in ΔG° for the latter. This feature is mainly due to the uncertainty in the control and measurement of p_{CO_2} .

The tendency of the $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ supercon-

ductor material towards carbonatization is largely due to the large content of the alkaline earth element. Thus, a similar behaviour is also expected for the rare earth-substituted analogues $\text{REBa}_2\text{Cu}_3\text{O}_{6+x}$. In all probability, $\text{YSr}_2\text{Cu}_3\text{O}_{6+x}$, if it exists, is less susceptible to carbonatization due to the reduced stability of SrCO_3 .

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References

1. Nakada, I., Sato, S., Oda, Y. and Kohara, T. *Jpn. J. Appl. Phys.* 26 (1987) L697.
2. Yan, M. F., Barns, R. L., O'Bryan, H. M., Jr., Gallagher, P. K., Sherwood, R. C. and Jin, S. *Appl. Phys. Lett.* 51 (1987) 532.
3. Rosamilia, J. M., Miller, B., Schneemeyer, L. F., Waszczak, J. V. and O'Bryan, H. M., Jr. *J. Electrochem. Soc.* 134 (1987) 863.
4. Kishio, K., Shimoyama, J., Hasegawa, T., Kitazawa, K. and Fucki, K. *Jpn. J. Appl. Phys.* 26 (1987) L1228.
5. Renault, A., Burdett, J. K., and Pouget, J.-P. *J. Solid State Chem.* 71 (1987) 587.
6. Kistenmacher, T. J. *Inorg. Chem.* 26 (1987) 3649.
7. Monod, P., Ribault, M., D'Yvoire, F., Jegoudez, J., Collin, G. and Revcolevschi, A. *J. Phys. (Paris)* 48 (1987) 1369.
8. Manthiram, A., Swinnea, J. S., Sui, Z. T., Steinfink, H. and Goodenough, J. B. *J. Am. Chem. Soc.* 109 (1987) 6667.
9. Strobel, P., Capponi, J. J., Marezio, M. and Monod, P. *Solid State Commun.* 64 (1987) 513.
10. Gabelica, Z., Derouane, E. G., Vigneron, J. P., Lambin, P., Renier, M., Lucas, A. A., Deconinck, G., Bodart, F. and Demortier, G. *Solid State Commun.* 64 (1987) 1221.
11. Smith, D. W. *J. Chem. Educ.* 64 (1987) 480.
12. Southard, J. C. and Royster, P. H. *J. Phys. Chem.* 40 (1936) 435.

13. Bäckström, H. J. L. *Z. Phys. Chem.* 121 (1926) 289.
14. Gleixner, R. A. and Chaug, Y. A. *Metall. Trans., B* 16 (1985) 743.
15. Ersson, N. O. *Program CELLKANT*, Chemical Institute, Uppsala University, Uppsala, Sweden 1981.
16. Francois, M., Walker, E., Jorda, J.-L. and Yvon, K. *Solid State Commun.* 63 (1987) 1149.
17. Hewat, A. W., Capponi, J. J., Chaillout, C., Marezio, M. and Hewat, E. A. *Solid State Commun.* 64 (1987) 301.
18. Garbaskas, M. F., Arendt, R. M. and Kasper, J. S. *Inorg. Chem.* 26 (1987) 3191.
19. Kajitani, T., Oh-Ishi, K., Kikuchi, M., Syono, Y. and Hirabayashi, M. *Jpn. J. Appl. Phys.* 26 (1987) L1144.
20. Fjellvåg, H., Karen, P. and Kjekshus, A. *Acta Chem. Scand., Ser. A* 41 (1987) 283.
21. Jorgensen, J. D., Beno, M. A., Hinks, D. G., Soderholm, L., Volin, K. J., Hitterman, R. L., Grace, J. D., Schuller, I. K., Segre, C. U., Zhang, K. and Kleefisch, M. S. *Phys. Rev. B* 36 (1987) 3608.
22. Jorgensen, J. D., Veal, B. W., Kwok, W. K., Crabtree, G. W., Umezawa, A., Nowicki, L. J. and Paulikas, A. P. *Phys. Rev. B* 36 (1987) 5731.
23. Cava, R. J., Batlogg, B., Chen, C. H., Rietman, E. A., Zahurak, S. M. and Werder, D. *Phys. Rev. B* 36 (1987) 5719.
24. Freitas, P. P. and Plaskett, T. S. *Phys. Rev. B* 36 (1987) 5723.
25. Barin, I. and Knacke, O. *Thermochemical Properties of Inorganic Substances*, Springer, Berlin-Heidelberg-New York 1973, pp. 77, 79, 163, 174, 181 and 711.
26. Barin, I., Knacke, O. and Kubaschewski, O. *Thermochemical Properties of Inorganic Substances, Supplement*, Springer, Berlin-Heidelberg-New York 1977, p. 679.
27. Wagman, D. D., Evans, W. H., Parker, V. B., Schumm, R. H., Halow, I., Bailey, S. M., Churney, K. L. and Nuttal, R. L. *The NBS Tables of Chemical Thermodynamic Properties; J. Phys. Chem. Ref. Data, Suppl.* 2 (1982) Vol. 11, pp. 154, 216 and 286.

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