

Oxycarbonates in the Y(O/CO₃)–Ba(O/CO₃)–Cu(O/CO₃) System

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The Ba-rich oxides in the Y(O)–Ba(O)–Cu(O) system have a high affinity toward CO₂, which is manifested in the formation of oxycarbonates. The pseudoternary system Y(O/CO₃)–Ba(O/CO₃)–Cu(O/CO₃) is investigated at temperatures between 780 and 1000°C in atmospheres containing oxygen and ~5, ~40, and ~350 ppm CO₂. Three oxycarbonates are identified: (1) Tetragonal Y₂Ba₃(CO₃)_uO_{6-u}, $u \approx 1$, with $a = 438.63(4)$ and $c = 1185.9(2)$ pm. (2) Y_{1+x}Ba₈Cu_{4+z}(CO₃)_uO_{11+w}, $u \approx 2$, $x \in (0, 0.3)$, $z \in (0, 0.4)$, and $w \in [0.05(2), 1.08(2)]$ for $x = z = 0$. Its structure, which accommodates vacancies on both cationic and anionic sites, is closely related to (the hypothetical perovskite) BaCuO₃ and represents the actual composition for the so-called “other perovskite phase” claimed for the Y(O)–Ba(O)–Cu(O) system. (3) Tetragonal YBa₂Cu₃(CO₃)_uO_{7-u-v} with $a = 387.38(3)$ and $c = 1161.2(4)$ pm for $u \approx 0.2$, $v \approx 0.1$, when carbonate-saturated at 800°C and oxygen-saturated at 320°C in an ~40 ppm CO₂ containing oxygen atmosphere. Structurally, this oxycarbonate is derived from YBa₂Cu₃O₇ by replacement of some oxygens by carbonate groups, and this phase represents the actual composition of the so-called “high-oxygen tetragonal 123 phase,” which is nonsuperconducting down to 4 K. The thermal stability of the oxycarbonates in oxygen with $p_{\text{CO}_2} \approx 4$ Pa decreases with decreasing Ba content from 960°C for (1) to 940°C for (2) and to 830°C for (3). © 1991 Academic Press, Inc.

Introduction

Certain binary or multicomponent metal oxides become superconducting when they are subjected to “doping” by holes. There are two usual ways of introducing the holes—substitution by a lower valent, more electropositive metal or addition of more nonmetals. Both approaches lead to a higher formal oxidation state for the less electropositive parent metal, the stabilization of which requires participation of cations with low polarizability. These requirements specify a highly electropositive metal which in turn introduces an enhanced Lewis basicity to the oxygen atoms. As a result, the oxide becomes more reactive toward Lewis

acids (e.g., Al₂O₃, SO₂, SiO₂, CO₂) and even H₂O. Carbon dioxide is of considerable importance in this connection, since CO₂ is a common component in various chemical environments and in particular because some common oxide preparation routes involve carbon containing compounds.

The high temperature reaction of CO₂ gas with YBa₂Cu₃O_{9-δ} leads upon completion to BaCO₃ and copper and yttrium oxides (1, 2). However, under certain conditions, oxycarbonates may form, prior to the complete carbonatization. The formation of (pseudo)ternary barium yttrium oxycarbonates was first recognized by DeLeeuw *et al.* (3), and about simultaneously, the formation of (pseudo)quaternary barium yttrium

copper oxycarbonates was indicated (4–6). The phase which is usually referred to as “the other perovskite,” because its location in the phase diagram is subject to considerable ambiguity in the literature data, is also suspected to be stabilized by carbonate. The composition of $Y_2Ba_8Cu_{4.25+z}O_{15+w} \cdot uCO_2$ was proposed by Roth *et al.* (4), and $Y_{1+x}Ba_8Cu_{4+z}O_{13+w} \cdot uCO_2$ by Fjellvåg *et al.* (5). A tentative Y(O/CO₃)-Ba(O/CO₃)-Cu(O/CO₃) pseudoternary phase diagram, reported by Karen *et al.* (6), involves also an oxycarbonate at the “123” composition and an analogous phase was indicated by Lindemer *et al.* (7).

In this study, the three oxycarbonate phases are further characterized by chemical analyses and powder X-ray diffraction (PXD), and discussed in relation to Y(O/CO₃)-Ba(O/CO₃)-Cu(O/CO₃) phase diagrams.

Experimental

Synthesis. Samples were prepared by multiple firing of precursors obtained by liquid mixing to citrate gels. The components, viz., Y₂O₃ (5N, Megon), BaCO₃ (reagent grade, Merck) and CuCO₃ · Cu(OH)₂ · 0.5H₂O (Riedel de Häen), were dissolved in boiling citric acid monohydrate (in a ratio of 0.8 mol/valence of the metals per mole of the acid). The resulting clear blue citrate gel was dried at 180°C, incinerated in air, milled, pelletized, and subsequently fired for 30 h at temperatures between 780 and 1000°C in a corundum boat under flow of purified oxygen (by CuO at 600°C and a KOH column at ambient; ~5 ppm CO₂), commercial oxygen (~40 ppm CO₂), or air (~350 ppm CO₂) for 20 hr. The firings were repeated at least three times (with intermittent rehomogenizations in an ultrafine agate vibration mill) until phase purity or no change in phase content and no improvement in the order/disorder characteristics (as indicated by line broadening) were seen

by PXD. The final oxidation was carried out at 320°C, and its complete and reproducible course was ascertained using loosely pressed pellets of a coarsely powdered product.

Carbon dioxide content analysis. Carbon in the samples, present as carbonate ions, was thermally released at 1100°C as CO₂ into flowing oxygen, and absorbed in a specified amount of Ba(OH)₂. The excess of the barium hydroxide was then titrated by 0.1 M kalium hydrogenphthalate, KHC₈H₄O₄.

Oxygen content control and analysis. The oxygen content in the samples was varied using controlled deoxidation by Ti powder (100- to 150-μm fraction, Koch-Light) or by a Cu/Cu₂O mixture in closed quartz ampoules. The precisely weighed amount of the Ti getter in the ampoule was heated for 48 hr at 750°C while the sample part of the ampoule was kept at 450°C. In a following step, the sample part was heated at 320°C for 24 hr to ensure oxygen homogeneity throughout the sample. The Cu/Cu₂O getter was used in excess, and the degree of deoxidation could be varied within certain limits by controlling the temperature (between 750 and 800°C), while other conditions were as above.

The oxygen content in the products was determined iodometrically. The analysis is based on comparison of the total oxidative capacity of the solid with that of Cu²⁺ obtained after reduction of the solid with HCl. The prereduced Cu²⁺ solution was obtained by dissolving approximately 0.15 g of the sample in ~20 ml 1 M HCl. The solution was thereafter evaporated until the appearance of crystals and then redissolved in water. The iodine released after adding ~1 g of KI in 20 ml water was titrated by 0.1 M Na₂S₂O₃. Before the end point, 2 ml of a 10% solution of NH₄SCN was added, and the exact end point was determined by means of a soluble starch indicator. In order to determine the total oxidative power, ~0.1 g of a finely milled sample was first sus-

pended in a solution of ~ 1 g KI in 20 ml water, the flask was then filled with Ar, and 8 ml of 1 M HCl was added. After 5 min of ultrasound agitation, the completely released iodine was titrated. The accuracy of the determinations is, in units of the formal oxidation state of copper, ± 0.01 .

Analysis of the sum of oxygen and carbon dioxide. As check analyses, sums of oxygen and carbon dioxide contents were also determined (in the cuprate samples only), using hydrogen-thermal reduction. The powdered sample of ~ 0.5 g, placed in a Pt boat, was reduced in H_2 ($\geq 99.99\%$, AGA Norgas; flow rate 250 ml/min) for 6 hr. After cooling in a flow of pure Ar ($\geq 99.99\%$, AGA Norgas; flow rate 70 ml/min), the sample was immediately transferred into a dry atmosphere and weighed. The complete reduction and decomposition into Y_2O_3 , BaO, and Cu were verified by PXD phase analysis.

Powder X-ray diffraction. All samples were checked for homogeneity and characterized by PXD. Guinier–Hägg cameras, $CuK\alpha_1$ radiation, and Si as internal standard were used. Position and intensity measurements of the reflections were carried out using a Nicolet L18 film scanner controlled by the SCANPI program (8) system. Trial and error indexing of the PXD patterns was done with the help of the TREOR program (9). Unit cell dimensions were obtained by least squares refinements using the CELLKANT program (10).

Formation; Chemical and Structural Properties

Phase diagrams of the $Y(O/CO_3)$ – $Ba(O/CO_3)$ – $Cu(O/CO_3)$ pseudoternary system at 800 and 900°C, as obtained for a large number of samples, after multiple firings of their citrate precursors in 1 atm O_2 with ~ 40 ppm CO_2 , are shown in Fig. 1.

The least thermally stable oxycarbonate, with the lowest BaO content, is situated at

the 123¹ point of Fig. 1. Carbon dioxide analyses of independent samples indicate a presence of 0.05 to 0.1 CO_2 per Ba, while the formal Cu valence remains slightly less than 2.30 (by iodometry). The alternative possibility of a presence of up to ~ 7 wt% of $BaCO_3$ in the samples was ruled out by PXD. Two comparative experiments are performed to ensure the reliability of the carbon dioxide analyses. First, parallel samples of the 124 phase were analyzed, giving less than 0.01 CO_2 per Ba. The same low CO_2 content was found when the carbonated 123 phase was thermally decomposed to pure orthorhombic 123 at 900°C in the second series of experiments. The formula $YBa_2Cu_3(CO_3)_{0.2}O_{6.7}$ applies to the product formed at 800°C in 40 ppm CO_2 in oxygen (100 kPa) atmosphere.

This minute amount of carbonate ions in the structure is nevertheless sufficient to convert the symmetry from orthorhombic to tetragonal as seen by PXD. Compared with the parent oxide, the *ab* base of the unit cell is increased by 1.13% and the *c* axis is contracted by 0.58%. The unit cell parameters of $YBa_2Cu_3(CO_3)_{0.2}O_{6.7}$ are $a = 387.38(3)$ and $c = 1161.2(4)$ pm, PXD data for identificational documentation being given in Table I. Observed broadenings of the PXD reflections support structural disorder presumably due to random orientation of the carbonate triangles throughout the tetragonal structure. As implied by the formula, carbonate ions *replace* some of the oxygen atoms, contrary to the alternative possibility that some oxygen vacancies could have become filled. The most probable structural location for the carbonate ion is near the O(1) site in the square chains of the parent phase, where the CO_3^{2-} would be bridging the gap between two Ba^{2+} . Based

¹ We will frequently make use of shorthand such as 123 when the relative cationic proportions of a phase rather than its complete formula are of importance.

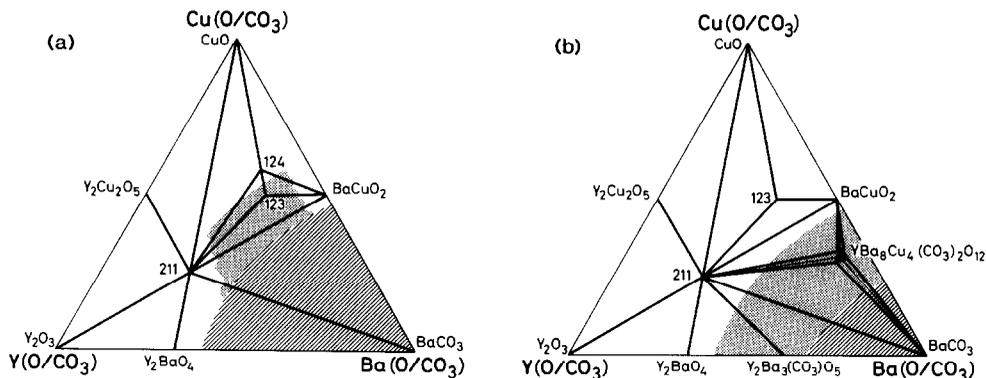


FIG. 1. Phase compatibilities in the $Y(O/CO_3)$ - $Ba(O/CO_3)$ - $Cu(O/CO_3)$ pseudoternary system, as seen by PXD after repeated firings of samples at (a) 800 and (b) 900°C in 1 atm oxygen containing ~ 40 ppm CO_2 . Phenomenological frontiers of oxycarbonate stability are shown by a dotted shading, those of carbonate stability by line-shading. Only indicative formulae are given.

on the size of the constituents it is now possible to propose atomic coordinates (Table II) for the carbonated 123 phase and this model may be regarded as semiquantitatively confirmed by PXD pattern calculations.

An interesting compositional feature of the carbonated 123 phase is that accommodation of cations of rather small "size" at the Ba site is promoted by the carbonati-

zation, viz., is easier than for the parent oxidic phase. Thus even Y may partially replace Ba, and an extended solid solution $Y(Ba_{1-y}Y)_2Cu_3(CO_3)_{0.2}O_{6.7+y}$, $y \in (0, 0.2)$, is obtained. Also appreciable amounts of, say, Ca and Hg may replace Ba in the carbonated 123 phase. However, even at a temperature as low as 780°C, impurity phases, particularly Y_2BaCuO_5 , start to emerge after a few repeated firings of $Y(Ba_{1-y}Y)_2Cu_3(CO_3)_{0.2}O_{6.7+y}$ in oxygen with ~ 40 ppm CO_2 . The course of the firing process, starting from a carbonate-rich material, suggests that higher CO_2 concentrations and lower temperatures during the preparation tend to stabilize the carbonated, Y-for-Ba substituted phase. However, the said conditions hinder the formation kinetically, and impure products are consequently obtained. For $y = 0.2$ in the above formula, unit cell parameters $a = 387.7(2)$ and $c = 1157.3(13)$ pm are found, indicating a further contraction of c due to the exchange of the large Ba with the smaller Y. Such solid solutions have variously been reported in the literature (11, 12), without the realization that the products are really oxycarbonates. Similarly, several reports

TABLE I
PXD DATA FOR $YBa_2Cu_3(CO_3)_{0.2}O_{6.7}$

d (pm)	hkl	I_r
1167	001	1
584	002	1
388	100,003	8
322	102	2
274	103	100
248	112	1
232.2	005,104	5
223.6	113	8
193.6	200	20
173.2	210	4
158.1	213,116	28
148.7	205,214	2
137.0	206,220	8

TABLE II

PROPOSED ATOMIC COORDINATES AND SITE OCCUPANCIES FOR $\text{YBa}_2\text{Cu}_3(\text{CO}_3)_{0.2}\text{O}_{6.7}$; SPACE GROUP $P4/mmm$

Atom	Site	x	y	z	n
Y	1d	0.5	0.5	0.5	1
Ba	2h	0.5	0.5	0.165	1
Cu(1)	1a	0.0	0.0	0.0	1
Cu(2)	2g	0.0	0.0	0.362	1
O(1)	2f	0.0	0.5	0.0	0.35
O(2)	2g	0.0	0.0	0.151	1
O(3)	4i	0.0	0.5	0.379	1
C	4n	0.250	0.5	0.0	0.05
O(4)	4n	-0.050	0.5	0.0	0.05
O(5)	8p	0.413	0.233	0.0	0.05

(13–16) on tetragonal variants of the 123 phase with an “oxygen” content of ~ 7 likely deal with the oxycarbonate phase.

More thermally stable oxycarbonates are formed in the region closer to the Ba-corner of the phase diagram (Fig. 1). One of these is “the other perovskite phase,” located at 184, with a homogeneity region extending toward both Y and Cu. Based on the quantitative analyses, specified in terms of the metal oxides (6) and carbon dioxide, the formula $\text{Y}_{1+x}\text{Ba}_8\text{Cu}_{4+z}(\text{CO}_3)_u\text{O}_{11+w}$, with $u \approx 2$, $x \in (0, 0.3)$, and $z \in (0, 0.4)$, is found to describe the composition of this oxycarbonate. The content of bonded carbonate may apparently also vary, say, within $u \in (1.5, 2.5)$, depending on the temperature and the gas phase conditions ($p_{\text{CO}_2}/p_{\text{O}_2}$) during the preparation, but a separate study of the equilibrium would be necessary to specify the conditions more closely. The oxygen content may be varied in a manner similar to that established for the 123 phase, i.e., there is a pressure–temperature equilibrium between oxygen gas and vacancies in the solid. The oxygen-saturated 184 phase has $w = 1.08(2)$. Deoxidation at 800°C in equilibrium with $\text{Cu}/\text{Cu}_2\text{O}$, which is capable of reducing 123 to $\text{YBa}_2\text{Cu}_3\text{O}_6$, leads to $w = 0.05(2)$. If additional metal atoms (x and/or $z > 0$) are introduced into the vacant cationic

sites, the range of w is shifted correspondingly to higher values. Three bulk samples of the $\text{Y}_{1+x}\text{Ba}_8\text{Cu}_{4+z}(\text{CO}_3)_2\text{O}_{11+w}$ solid solution are prepared close to the composition limits ($x = z = 0.00$; $x = 0.33$, $z = 0.00$; and $x = 0.00$, $z = 0.33$) in oxidized ($w = 1.08$, 1.62 and 1.52 , respectively) and reduced ($w = 0.06$, 0.68 and 0.44 , respectively) forms, and their PXD data are listed in Table III. The observed, extensive broadening of some of the reflections (see the half-width of the 111 reflection; Table III) indicates the occurrence of a structural disorder in addition to the distortions of the ideal perovskite arrangement ($a \approx 404$ pm). This complicates the choice of the appropriate unit cell for description of the involved superlattice orderings. Possible (tetragonal or orthorhombic) unit cells may best be judged from the (still) poorly resolved splittings of the 100 and 200 reflections according to the simple approximate indexing, based on the pseudocubic subcell (Table III).

The 184 oxycarbonate decomposes thermally above 940°C . The decomposition is rather slow and proceeds apparently via a number of compositionally closely spaced, intermediate phases. The decomposition products at 1000°C could not be identified with any of the oxidic phases which DeLeeuw *et al.* (3) report in the vicinity of

TABLE III
 PXD DATA FOR OXIDIZED AND REDUCED Y_{1+x}Ba₈Cu_{4+z}(CO₃)₂O_{11+w}

$h^2 + k^2 + l^2$	$x = 0.00, z = 0.00$				$x = 0.33, z = 0.00$				$x = 0.00, z = 0.33$			
	$w = 1.08$		$w = 0.06$		$w = 1.62$		$w = 0.68$		$w = 1.52$		$w = 0.44$	
	d (pm)	I_r	d (pm)	I_r	d (pm)	I_r	d (pm)	I_r	d (pm)	I_r	d (pm)	I_r
1/4	805	5	807	10	803	3	803	7	804	5	809	7
1	409	2	407	9	404-416	6	407	8	406-412	3	410	2
	403	8	404	5	403	3	403	4	404	7	406	8
2	287.4	45	287.0	102	287.6	43	288.3	36	287.7	40	288.2	52
	286.0	38			285.8	25	286.7	41	285.9	28		
3	234.2	10	234.9	10	234.4	10	234.9	10	234.4	10	235.0	10
13/4	224.2	2	224.7	4	224.5	2	224.7	3	224.4	2	225.4	5
4	202-206	3	203.5	8	203-208	4	204-208	5	203-207	6	203-206	6
	201.8	9	201.9	5	202.1	5	203.5	5	202.0	11	202.8	14
					201.6	7	201.7	4				
5	180-183	6	180-184	6	182-185	2	182-184	5	182-184	3	182-183	3
					181.2	2	181.1	2	181.0	4	181.5	4
					180.7	2						
6	166-167	3	166.2	13	166-169	6	167-169	7	166.6	4	166.7	6
							166.2	7				
	165.4	15	165.9	12	165.4	18	165.4	7	165.4	19	165.9	18
29/4	150.5	1	151.0	2	150.5	2	151.0	2			151.0	3
HFV:	1.5		1.6		2.4		2.1		1.4		1.4	

Note. Indexing relates to a single perovskite; indices of superstructure reflections come out as fractions. Intensities are related to $I = 10$ for the $h^2 + k^2 + l^2 = 3$ reflection, the halfwidth of which (HFV, in pm) is used as a measure for the degree of occupational disorder, free from effects of the perovskite deformation.

the 184 composition. Of these, only 143 is readily formed above 960°C from carbonaceous starting materials in purified oxygen ($p_{\text{CO}_2} \approx 0.5$ Pa), whereas the phases 152, 385, and Ba₂CuO₃ are not obtained even for repeated firings at 1000°C. This indicates that an array of closely related oxycarbonate structures may be obtained between the 184 oxycarbonate and the pure oxide phases, but that the preparational conditions for these may be sensitive to details in the procedure.

The most stable oxycarbonates are expected to be found along the Y-Ba-O pseudobinary line in Fig. 1. However, also in this case, difficulties in identification are caused by the presence of a large variety of phases in this part of the phase diagram, see also Kvestroo *et al.* (17). Moreover, the temperatures required for complete decomposition of the barium carbonate-rich starting mixtures may have to compete with a partial

melting as well as evaporation of BaO (18). As a result of this, many ternary barium oxides described in the literature may not have been obtained in a phase-pure state, and hence their compositional identity (based on, say, contaminated PXD data) may be of rather limited value.

No indication of any oxycarbonate formation was obtained for the most Ba-poor phase Y₂BaO₄, which is readily obtained phase-pure from carbonaceous starting materials at 940°C in purified oxygen ($p_{\text{CO}_2} \approx 0.5$ Pa).

Our attempts to obtain a phase with the 220 (Y₂Ba₂O₅) or 330 (Y₃Ba₃O_{7.5}) composition (17, 19) resulted in mixtures, containing ~40 wt% of Y₂BaO₄ (as estimated from the PXD data), thus confirming the results concerning the phase impurity in Refs. (17, 19). This strongly suggests that the 220 (330) composition is wrong. The reported thermal instability (17) of this presumed 220 (330)

phase speaks for CO₂ stabilization as proposed by DeLeeuw *et al.* (3). Based on a mole-balance estimate, the composition 230 was attempted as the more probable for this phase, resulting in an almost phase-pure product, with few weak impurity PXD reflections, which could be assigned to Y₂Ba₄O₇ (19) and Y₄Ba₃O₉ (17). The estimated sum of these impurities does not exceed ~10 wt%, and their amounts and compositions would account for the composition of the starting mixture. This leaves little space for speculations on a different low-integer stoichiometry for the major phase. Analyses of carbon dioxide content indicate 0.6 to 1.0 CO₂ per formula, which is thus specified as Y₂Ba₃(CO₃)_uO_{6-u}, $u \approx 1$. This phase is stable up to 960°C in purified oxygen ($p_{\text{CO}_2} \approx 0.5$ Pa). Reflections from the above-mentioned impurities are identified as main components in the PXD pattern for the decomposition product (at 1000°C), whereas all the reflections assigned to Y₂Ba₃(CO₃)O₅ have disappeared. This may be taken as a further indication that the proposed formula represents a good approximation to the actual composition of this oxycarbonate. The PXD pattern of Y₂Ba₃(CO₃)O₅ agrees with that in Ref. (17), and the derived (tetragonal) unit cell parameters are $a = 438.63(4)$ and $c = 1185.9(2)$ pm.

Generally, each of the oxycarbonates in question is stable in a narrow shell defined by the degree of basicity for the constituents (notably the BaO content), and delimited by the concentration of CO₂ in the surrounding atmosphere and the temperature. At lower BaO contents and CO₂ concentrations, as well as at higher temperatures, pure oxide phases become stable. For larger BaO contents, higher CO₂ concentrations or lower temperatures, BaCO₃ is stabilized next to the oxides. The crystal structures of the oxycarbonates are closely related to those of their parent oxide phases. This is particularly intriguing in the case of YBa₂Cu₃O₇, since the conversion into a nonsupercon-

ducting, but yet structurally very similar oxycarbonate, is induced even when comparatively minute amounts of carbonate replace oxygen.

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References

1. H. FJELLVÅG, P. KAREN, A. KJEKSHUS, P. KOFSTAD, AND T. NORBY, *Acta Chem. Scand. A* **42**, 178 (1988).
2. Y. GAO, K. L. MERKLE, C. ZHANG, U. BALACHANDRAN, AND R. B. POEPEL, *J. Mater. Res.* **5**, 1363 (1990).
3. D. M. DELEEUEW, C. A. H. A. MUTSAERS, C. LANGEREIS, H. C. A. SMOORENBURG, AND P. J. ROMMERS, *Physica C (Amsterdam)* **152**, 39 (1988).
4. R. S. ROTH, C. J. RAWN, F. BEECH, J. D. WHITLER, AND J. O. ANDERSON, in "Research Update 1988—Ceramic Superconductors II," (M. F. Yan, Ed.), p. 13, Amer. Ceram. Soc., Publ., Westerville, OH (1988).
5. H. FJELLVÅG, P. KAREN, A. KJEKSHUS, AND J. K. GREPSTAD, *Acta Chem. Scand. A* **42**, 171 (1988).
6. P. KAREN, O. BRAATEN, H. FJELLVÅG, AND A. KJEKSHUS, "Proceedings of the AMSAHTS'90 Conference", Greenbelt, MD (1990).
7. T. B. LINDEMER, C. R. HUBBARD, AND J. BRYNESTAD, *Physica C (Amsterdam)* **167**, 312 (1990).
8. P. E. WERNER, The Computer Programme SCANPI, Institute of Inorganic Chemistry, University of Stockholm, Sweden (1981).
9. P. E. WERNER, The Computer Programme TREOR-5 (1988) [see also *Z. Kristallogr.* **120**, 375 (1964)].
10. N. O. ERSSON, Programme CELLKANT, Chemical Institute, Uppsala University, Uppsala, Sweden (1981).
11. Z. IQBAL, F. REIDINGER, A. BOSE, N. CIPOLLINI, T. J. TAYLOR, H. ECKHARDT, B. L. RAMAKRISHANA, AND E. W. ONG, *Nature* **331**, 326 (1988).
12. A. M. UMARI, P. SOMASUNDARAM, L. GANAPATHI, AND C. N. R. RAO, *Solid State Commun.* **66**, 177 (1988).
13. H. FJELLVÅG, P. KAREN, AND A. KJEKSHUS, *Acta Chem. Scand. A* **41**, 283 (1987).
14. B. GUDMUNDSSON, H. WANG, R. A. NEISER, B. KATZ, H. HERMAN, AND M. SUENAGA, *J. Appl. Phys.* **67**, 2653 (1990).
15. C. N. R. RAO, R. NAGARAJAN, A. K. GANGULI,

- G. N. SUBBANNA, AND S. V. BHAT, *Phys. Rev. B Condens. Matter* **42**, 6765 (1990).
16. D. E. MORRIS, P. K. NARWANKAR, AND A. P. B. SINHA, *Physica C (Amsterdam)* **169**, 7 (1990).
17. W. KWESTROO, H. A. M. VAN HAL, AND C. LANGEREIS, *Mater. Res. Bull.* **9**, 1631 (1974).
18. R. H. LAMOREAUX, D. L. HILDEBRAND, AND L. BREWER, *J. Phys. Chem. Ref. Data* **16**, 419 (1987).
19. L. M. KOBVA, L. N. LYKOVA, AND E. V. ANTIPOV, *Zh. Neorg. Khim.* **28**, 724 (1983).