

Crystal Chemistry of Yttrium-Barium-Copper Oxycarbonate Ceramics

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The barium rich region of the Y-Ba-Cu-O-C system includes a tetragonal perovskite-like phase, which possesses a wide homogeneity region toward yttrium, copper and carbonate ion on the one hand, and toward oxygen, on the other hand. Accounting for vacancies (\square -vacancy) this phase could be described by the general formula per unit cell: $\{Ba_8\}[Y_{3-2z}Cu_{5-x}(CO_3)_n \square_{z+x-n}]O_{y=8y}$ (*). Here, cube-octahedral sites are represented in braces, while quasi-octahedral ones with proper octahedral (Y, Cu1), square (Cu2) and triangular (CO_3) configuration are shown in square brackets. The formula (*) was confirmed by full-profile Rietveld refinement based on X-ray diffraction data of $YBa_5Cu_2O_y$ (1-5-2 phase). Homogeneity region limits of the phase (*) at 960°C in air were determined to be $-0.33 \leq x \leq 1.80$, $0.33 \leq z \leq 2.00$, $0 \leq n \leq 3$.

Key words: Y-Ba-Cu-O-C system, Barium rich region, Perovskite-like phase, Homogeneity region, Oxycarbonates

I. Introduction

The barium rich region of the isothermal cross section (950-960°C, air) of the Y-Ba-Cu-O system phase diagram is characterized by a great number of phases, whose composition could be described as $Y_uBa_vCu_wO_y$. The most well known phases ("u-v-w") are "1-3-2",¹⁾ "3-8-5",²⁾ "1-8-4",³⁾ "1-6-3"^{4,5)} and "1-4-2".⁶⁾ They have a perovskite-like tetrago-

nal structure except for "1-6-3", which also has an orthorhombic modification. According to data^{4,5)}, this orthorhombic modification is formed only when preparation conditions exclude formation of carbonate ions. That means a possibility to prepare this phase as pure oxide. One more pure carbonate-free oxide is the cubic phase, "1-4-3". According to reference^{4,5)}, all other phases mentioned above are oxycarbonates and actually belong to the Y-Ba-Cu-O-C system. These phases are shown in Fig. 1; oxides and oxycarbonates are marked by circles and crosses, respectively.

An interesting fact is that all these oxycarbonates have similar unit cell constants in spite of differences in composition. Structure investigations done for the "3-8-5",²⁾ "1-8-4"³⁾ and "1-4-2"⁶⁾ resulted in similar models, that allow us to make an attempt to systematize the oxycarbonates in the Y-Ba-Cu-O-C system basing on the general crystal-chemical formula.

The present investigation was aimed to find a formula, defining compositions and structures of phases in the barium rich region.

II. Experimental Procedure

All studied compositions are shown in Table 1. Powders of Y_2O_3 , CuO and $BaCO_3$ with purity not less than 99,9% were mixed in various proportions in a FRITSCH planetary mill under isopropyl alcohol. These mixtures were pressed into pellets 14 mm in diameter and 4 mm thickness at 1 MPa and sintered at 960°C in air for 90 hours in a Nabertherm-type furnace. Products were analyzed by X-ray diffraction on the DRON-3.0 diffractometer (Cu $K\alpha$ radiation). Silicon was used as an internal standard ($a=0.54308(1)$ nm). Unit

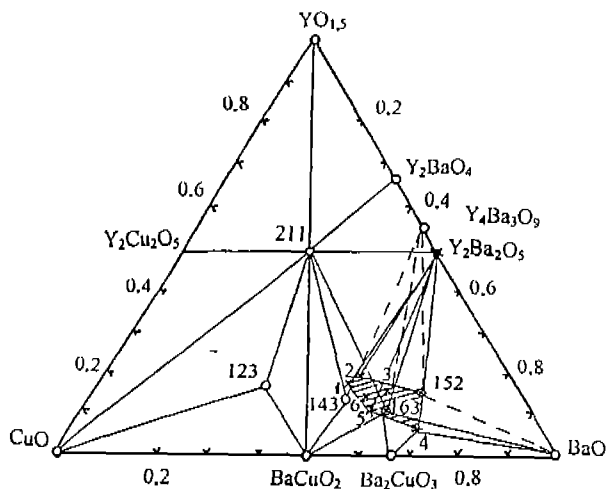


Fig. 1. Isothermal section of the Y_2O_3 -BaO-CuO-O and Y_2O_3 -BaO-CuO-O-C systems at 960°C. Here, oxides and oxycarbonates are shown as circles and crosses, respectively. Digits mark the compositions of oxycarbonates: 1-"1-3-2", 2-"3-8-5", 3-"1-4-2", 4-"1-8-4", 5-"1-4-2.5", 6-"1-6-3.5". Composition of an oxide phase is shown as 143, and two phases existing both as oxides and oxycarbonates are shown as 163 and 152. The region of the oxycarbonate phase stability is shown by shading.

Table 1. Compositions and Cell Constants of $Y_{3-x}Ba_8Cu_{n-x}(CO_3)_n \square_{z+x-n}O_{y+8y}$

N	Composition	z	x	n	$z+x-n$	$a, \text{\AA}$	$b, \text{\AA}$	$c, \text{\AA}$	$V, \text{\AA}^3$
1	1-8-4	2.0	1.0	3.0	0	8.123(1)	—	8.062(1)	532
2	1-6-3	1.67	1.0	3.0	-0.3	8.208(2)	8.118(1)	8.060(1)	537
3	1-6-3.5	1.67	0.33	1.3	0.7	8.227(2)	—	8.027(2)	543
4	1-5-2	1.4	1.8	3.0	0.2	8.183(1)	—	8.009(1)	536
5	1-4-2	1.0	1.0	1.0	1.0	8.188(1)	—	8.037(1)	539
6	1-4-2.5	1.0	0	1.0	0	8.202(1)	—	8.014(1)	539
7	1-3-2*	0.33	-0.33	0	0	8.213(1)	—	8.006(1)	540
8	1-4-3	1.0	-1.0	0	0	8.067(4)	—	—	525
9	3-8-5*	0	0	0	0	8.240(5)	—	8.004(4)	543

*Contains traces of the "1-4-3" type cubic phase.

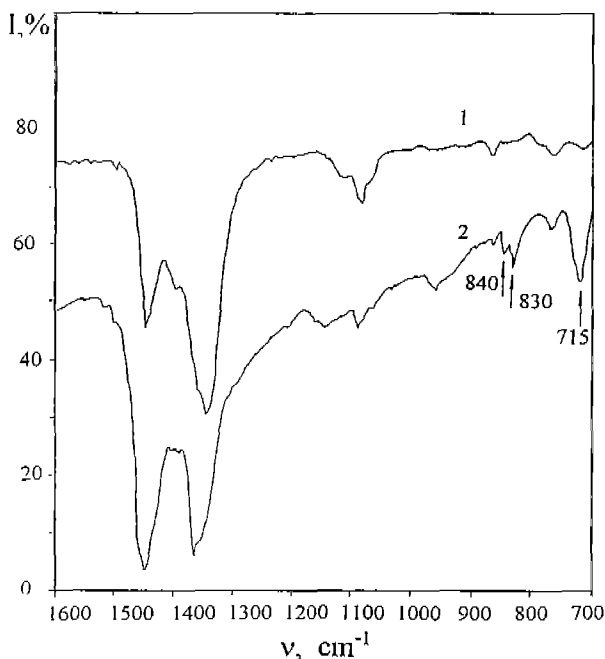


Fig. 2. Infra-red spectrum: 1-spectrum of vaseline oil; 2- spectrum of the phase $YBa_5Cu_2O_y(CO_3)_{1.883}$ ("1-5-2"). in vaseline oil.

cell constants were calculated by the PIRUM program⁷. X-ray powder data for Rietveld refinement were collected on a STOE diffractometer STADI-P (Cu $K\alpha_1$ radiation). Carbon content was determined by the LECO CS-225 analyzer. Infrared spectra were collected on the spectrometer SPECORD-75.

III. Results and Discussion

Unit cell parameters and volumes of studied phases are shown in Table 1. All the phases have a tetragonal structure with doubled perovskite-like cell, except for the "1-6-3" phase which has a pseudo-tetragonal structure with a weak orthorhombic distortion. As a rule, they contain carbonate ions. That was confirmed by infrared spectra. The one of $YBa_5Cu_2O_y(CO_3)_{1.88}$ ("1-5-2") is shown in Fig. 2. It was compared with a spectrum of barium carbonate⁸. Comparison of

Table 2. Structure Refinement Results for the Tetragonal Phase 1-5-2 ($P4/mmm$, $a=b=8.183(1) \text{\AA}$, $c=8.003(1) \text{\AA}$, $R_B=5.08\%$, $R_p=5.91\%$, $R_{wp}=9.38\%$, $R_{exp}=6.90\%$)

Atom	Position	x	y	z	Occupancy
C1	1a	0	0	0	0.99(8)
C2	2e	0	0.5	0.5	1.00(1)
Y1	2e	0	0.5	0.5	1.00(1)
Cu1	1b	0	0	0.5	0.99(2)
Cu2	1d	0.5	0.5	0.5	0.24(1)
Y2	1d	0.5	0.5	0.5	0.64(1)
Cu3	1c	0.5	0.5	0	1.01(2)
Cu4	2f	0	0.5	0	0.99(2)
C3	2f	0.5	0	0	0.99(2)
Ba	8r	0.25	0.25	0.2576(4)	7.98(3)
O1	4n	0.233(9)	0.5	0	3.3(1)
O2	4o	0.232(6)	0.5	0.5	4.0(1)
O3	2g	0	0	0.289(4)	2.06(8)
O4	4i	0.5	0	0.142(7)	2.05(3)
O5	2h	0.5	0.5	0.223(7)	2.0(1)
O6	4m	0.268(5)	0	0.5	3.8(2)
O7	4l	0.001(4)	0	0	2.87(6)

$B_{iso}=0.65(6) \text{\AA}^2$, profile parameters: $m_{pearson}=1.66(3)$, $u=0.17(1)$, $v=-0.05(1)$, $w=0.016(2)$, Asymmetry=-1.9(4).

the detected frequency oscillations was considered to be an argument of presence of carbonate ions CO_3^{2-} . The relative amount "n" of carbonate ions per unit cell for each composition is shown in Table 1. A description of the unit cell will be given below. The phase "1-5-2" structure parameters refined in space group $P4/mmm$ by means of a program version⁹ of full-profile Rietveld analysis are shown in Table 2. Experimental and difference ($I_{exp}-I_{calc}$) profiles and positions of X-ray diffraction peaks are shown in Fig. 3. According to the refinement, practically all cube-octahedral positions are occupied by barium ions. Octahedral positions are also completed, except one at (0.5 0.5 0.5) found to be randomly occupied by copper (Cu2) and yttrium ions, keeping 12% of the central sites vacant. Face centering positions (0 0.5 0.5), occupied by yttrium (Y1) and carbon (C2), and similar ones (0 0.5 0) in the basal plane, occupied by copper (Cu4) and

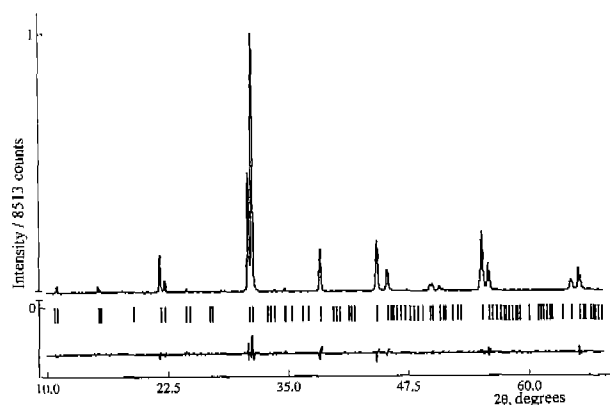


Fig. 3. Results of full-profile Rietveld refinement of $Y_{1.6}Ba_8Cu_{3.2}(CO_3)_3O_{11}$ ("1-5-2"). X-ray experimental data (above), difference curve (below) and peak positions (between).

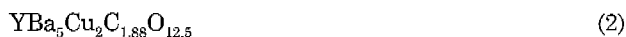
carbon (C3), are characterized by statistical distribution of the metal and carbon ions. Some types of ions have special sites: copper ions (Cu3) are localized in the center of the basal plane, Cu1 in the middle of the vertical edge (0 0 0.5) and carbon C1 on the origin.

Seven types of oxygen atoms forming both 12-fold coordinated and proper octahedral and square-planar arrangement around metal sites are shown in Table 2. Coordinates found for oxygen O1, O2, O3, O5, O6 and especially for O4 prove that all polyhedrons are considerably distorted. The coordinate "x" refined for oxygen O7 indicates an increase of electron density in the site (000) up to $C_{11} = 2.87 \times 10 + 0.99 \times 6 = 35$ e/site, that is close to the required for CO_3 configuration. Limitations of the X-ray diffraction method do not permit us to confirm such a configuration directly. Therefore we propose a structural model (Fig. 4) which is accurate in detail as far as the location of the centers of carbon complexes C1, C2 and C3.

More precise definition of the phase "1-5-2" composition according to data in Table 2 (occupation factors) results in the formula:



or recalculation on the basis of "1-5-2":



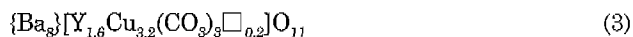
Assuming the oxycarbonate nature of the carbon complexes, these formula would be written as:



or



Considering nonequivalent crystallographic positions, occupied by various ions, and vacancies, the formula (1a) may be written as:



Here cube-octahedral and octahedral positions are shown

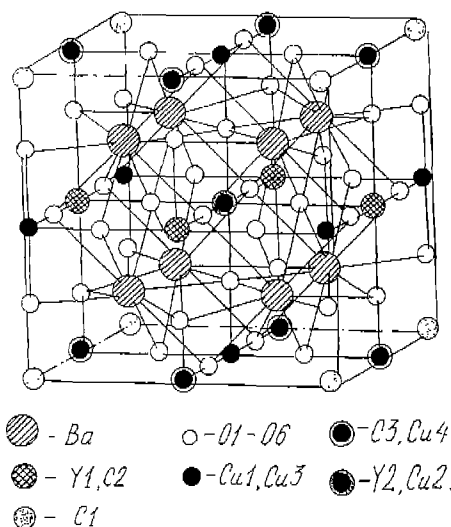
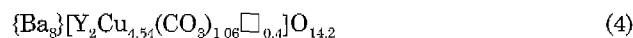
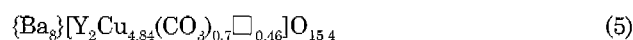


Fig. 4. Structure model of the tetragonal $Y_{1.6}Ba_8Cu_{3.2}(CO_3)_3O_{11}$ ("1-5-2").

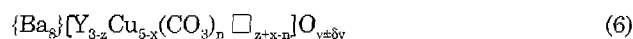
in braces and square brackets, respectively. The latter, indeed, includes both proper octahedral and (in case of copper ion Cu4) square planar positions and also (in case of CO_3 complexes) triangular planes. A way to localize the positions in a perovskite-like structure with space group $P4/mmm$ has been shown⁶⁾, where structure parameters of Y-Ba-Cu oxycarbonates with compositions "1-4-2.27" and "1-4-2.42" were refined by means of neutron diffraction. Results of these refinements, written in correspondence with the cell we obtain for "1-5-2" (see formula 3), lead to the following formulations:



and



Similarly, any oxycarbonate in Table 1 could be described by the general formula including 12-fold coordinated and quasi-octahedral positions:



Parameters z , x and n in the formula (6) for the studied compositions are shown in Table 1. The formula (6) permits us to represent these oxycarbonates as a unique phase with a wide homogeneity region for quasi-octahedral (including square and triangular) and oxygen positions. Not only do the contents of copper, yttrium, carbonate ions and vacancies in quasi-octahedral sublattice, but also the ways of their localization and site occupancies depend upon the overall composition of this phase. It affects the oxygen sublattice as well: only the cube-octahedral sublattice, occupied by eight barium ions, is completely filled.

Carbonate ion contents (n) which exceed the number of free quasi-octahedral positions, not occupied by yttrium and copper ($z+x$) was considered to be a condition terminating the tetragonal phase stability. That correlates with an

excess of carbonate ions in the "1-6-3" phase, which results in an orthorhombic distortion of the pseudo-tetragonal cell (see Table 1). The absence of carbon atoms in crystallographic sites completely filled by yttrium and copper ions, is another condition making the tetragonal phase unstable (6). This type of destabilization may result in three different cases:

- 1) increase in the lattice symmetry up to cubic (phase "1-4-3"⁴⁾;
- 2) traces of other phases (compositions "1-3-2" and "3-8-5");
- 3) formation of an orthorhombic phase with $\text{Sr}_3\text{Ti}_2\text{O}_7$ -type structure (compositions "1-6-3"⁴⁾ and "1-5-2"²⁾).

So the homogeneity region limits of the tetragonal oxycarbonate phase, the unit cell of which could be described by the formula (6) and are defined by the parameters:

$$0.33 < z \leq 2.0; \quad -0.33 < x \leq 1.80; \quad 0 < n \leq 3.$$

This region is shown on the isothermal cross section of the phase diagram of the Y_2O_3 -BaO-CuO-O-C system at 960°C in air (Fig.1), by shading.

IV. Summary

An isothermal cross section (960°C, air) of the phase diagram of the Y-Ba-Cu-O-C system in barium rich region was constructed. This region is characterized by a tetragonal perovskite-like phase. Content of yttrium, copper and carbonate ions for this phase could vary over wide limits while still keeping the barium content constant.

A general formula describing the unit cell of this phase was proposed based on full-profile Rietveld refinement of X-ray diffraction data of $\text{YBa}_5\text{Cu}_2(\text{CO}_3)_{1.88}\text{O}_y$ and on comparison of the results with already available structural models for other oxycarbonates in this system.

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