

SUPERCONDUCTING Cd AND Ca DOPED 123 PHASE IN $\text{Cd}_{0.8}\text{Ba}_2(\text{Y}_{0.7}\text{Ca}_{0.4})\text{Cu}_{3.5}\text{O}_y$

N. BALCHEV, V. KOVACHEV

*Institute of Solid State Physics, Bulgarian Academy of Sciences
1784 Sofia, Bulgaria*

J. THOMAS, W. BIEGER

*Institut für Festkörper- und Werkstofforschung Dresden
01171 Dresden, Germany*

K. KONSTANTINOV

*Institute of General and Inorganic Chemistry, Bulgarian Academy of
Sciences
1113 Sofia, Bulgaria*

B. KUNEV

*Institute of Catalysis, Bulgarian Academy of Sciences
1113 Sofia, Bulgaria*

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Abstract. A new Cd-containing superconductor with nominal composition of $\text{Cd}_{0.8}\text{Ba}_2(\text{Y}_{0.7}\text{Ca}_{0.4})\text{Cu}_{3.5}\text{O}_y$ and $T_c = 80$ K was synthesized and investigated. The obtained XRD pattern shows that the dominating phase is an orthorhombic 123. It was shown that the presence of Cd and Ca facilitates the 123 phase formation. The results of the EDX analysis on SEM and TEM have shown that the distribution of the Cd and Ca in the samples is inhomogeneous. The two elements enter the 123 phase in most of the investigated crystals and form a new Cd-Ba-Y-Ca-Cu-O superconducting compound.

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1. Introduction

Since the discovery of the high- T_c superconductivity (HTSC) [1] many layered superconducting copper oxide compounds have been synthesized and investigated. Cadmium is an appropriate candidate for including in the superconducting systems. It is a stable divalent element with an ionic radius (1.09 Å) between those of Y^{3+} (1.04 Å) and Ca^{2+} (1.14 Å). For the last few years we have carried out a broad search for new

Cd-containing superconducting systems. Recently we have synthesized and investigated a new multiphase $\text{CdBa}_2(\text{Y}_{0.3}\text{Ca}_{0.7})\text{Cu}_2\text{O}_y$ superconductor with T_c up to 103 K [2]. However, unlike the Hg-based 1212 analogue [3], the minor superconducting phase obtained cannot be easily identified. The new superconductor chemical composition differs from the nominal one presumably because cadmium is an inert element and cannot be easily incorporated into the lattice structure of the superconductor [4]. A possible issue for further study might be to synthesize and investigate some Cd-containing superconducting compound found by the EDX analysis in [2]. The purpose of the present work is to obtain this compound in the system Cd-Ba-Y-Ca-Cu-O as a dominating superconducting phase. Investigating different compounds in Cd-Ba-Y-Ca-Cu-O more general aim of this work is to create Cd-12($n-1$) n homologous series similar to those of the Bi, Tl and Hg-based systems or to obtain a Cd and Ca substituted YBCO. This possibility is interesting not only because it is not investigated but because Iguchi et al. [5] have reported a high T_c anomaly (up to 105 K) in multiphase Cd-doped $\text{YBa}_2\text{Cu}_3\text{O}_y$. The obtained high values of T_c were metastable. It may be expected that the high T_c could be stabilized with an additional Ca substitution since Ca is readily incorporated in the 123 structure [6, 7].

In this work a new Cd-containing compound with nominal composition $\text{Cd}_{0.8}\text{Ba}_2(\text{Y}_{0.7}\text{Ca}_{0.4})\text{Cu}_{3.5}\text{O}_y$ was synthesized and investigated. The dominating superconducting phase was identified as an orthorhombic 123 phase. It was shown that the presence of Cd and Ca facilitates the 123 phase formation. The EDX analysis on SEM and TEM showed that the distribution of the two elements is inhomogeneous. The Cd and Ca are incorporated into the most of the investigated crystals and form a five-component compound in the system Cd-Ba-Y-Ca-Cu-O.

2. Results and Discussion

The investigated samples with nominal composition $\text{Cd}_{0.8}\text{Ba}_2(\text{Y}_{0.7}\text{Ca}_{0.4})\text{Cu}_{3.5}\text{O}_y$ were prepared by a solid state reaction in oxygen from starting materials CdO, BaCO_3 , Y_2O_3 , CaCO_3 and CuO each with purity over 99%. They were mixed, homogenized and pressed into pellets. The latter were sintered at 850–950 °C for 3–20 h and cooled in the furnace. The heating rate was 150 °C/min. In some cases a preheating of the mixture at 800 °C for 16 h was included. X-ray diffraction (XRD) was used to examine the samples using a TUR-M62 diffractometer. A SEM analysis was performed on the pellets using a Philips XL30 device including an Energy Dispersive X-ray analysis (EDX). A TEM-EDX analysis was also performed by using a Philips CM20 FEG device.

Figure 1 shows the powder XRD pattern of a sample with nominal composition $\text{Cd}_{0.8}\text{Ba}_2(\text{Y}_{0.7}\text{Ca}_{0.4})\text{Cu}_{3.5}\text{O}_y$, synthesized at 940 °C for 6 h in flowing oxygen. The same reproducible result is obtained if the synthesis is carried out at 900 °C for 16 h or if a preliminary step (800 °C, 16 h) is included. The presence of a dominating phase with CdO and BaCuO_2 as impurities may be seen in the figure. A careful examination of the XRD reflections shows that this is not the expected 1212 phase. Also, the double center perovskite structure in $\text{Cd}_{0.3}\text{Ba}_2\text{Cu}_{0.7}\text{O}_3$ reported in [8] was not found.

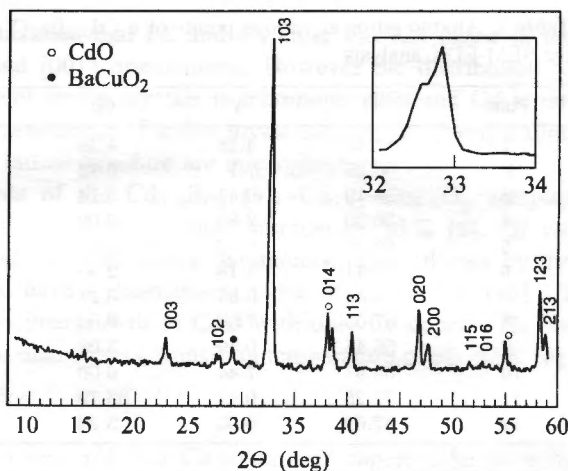


Fig. 1. XRD pattern of a $\text{Cd}_{0.8}\text{Ba}_2(\text{Y}_{0.7}\text{Ca}_{0.4})\text{Cu}_{3.5}\text{O}_y$ sample

The inset in the figure confirms that the obtained 123 phase is still orthorhombic. The authors of [4] have shown that a part of Cd is incorporated into the lattice structure in spite of the presence of CdO in the XRD pattern. In our case the lack of Ca-containing compound indicates a Ca substitution in the main 123 phase. This delicate moment will be discussed later. Also our synthesis time is significantly reduced in comparison with [4] — from 36 to 6 hours. A dominating phase is obtained even if the synthesis time is reduced to 3 hours. This result shows that the presence of Cd and Ca facilitates the 123 phase formation. From the XRD pattern the lattice parameters of the orthorhombic Cd and Ca containing sample ($a_0 = 3.820 \text{ \AA}$, $b_0 = 3.891 \text{ \AA}$, $c_0 = 11.704 \text{ \AA}$) were calculated. For comparison an undoped $\text{YBa}_2\text{Cu}_3\text{O}_y$, synthesized at the same conditions, has $a = 3.816 \text{ \AA}$, $b = 3.888 \text{ \AA}$ and $c = 11.664 \text{ \AA}$. It may be seen that all the lattice parameters of the orthorhombic Cd and Ca-containing sample increase, i. e. a substitution probably occurs. The calculated lattice parameters can be compared with those obtained by other authors. For example a_0 and b_0 are similar to those for the only Cd-doped 123, but c_0 is larger [5].

In order to obtain the chemical composition of the orthorhombic 123 phase, as well as to check whether Cd and Ca are present in the microcrystals, a SEM-EDX analysis was performed on a sample. The result of the EDX analysis at different points is given in Table 1. The calculations showed that the point 1 has a chemical composition, close to the nominal one. The points 2, 4, 5, 7, 8 and 10 correspond to a stoichiometric ratio $\text{Y}:\text{Ba}:\text{Cu}=1:2:3$ with low Cd and Ca substitution. The remaining points do not refer to a 123 stoichiometry. This result shows that the sample is still inhomogeneous and in some points Cd is not present (4, 8, 10). To our opinion the strong Cd and Ca deficiency in comparison with the nominal composition could be avoided by using a synthesis in a sealed environment.

In order to obtain information for the local incorporation of Cd and Ca along the different crystallographic zones, a TEM investigation was performed to a powdered $\text{Cd}_{0.8}\text{Ba}_2(\text{Y}_{0.7}\text{Ca}_{0.4})\text{Cu}_{3.5}\text{O}_y$ sample. Figure 2 shows the selected area electron diffraction (SAED) patterns of the sample along the $[331]$ (a) and $[12\bar{1}]$ (b) zone axes.

Table 1. Atomic ratios at various points of a $\text{Cd}_{0.8}\text{Ba}_2(\text{Y}_{0.7}\text{Ca}_{0.4})\text{Cu}_{3.5}\text{O}_y$ sample, according to the SEM-EDX analysis

Point	O	Y	Cd	Ca	Ba	Cu
1	57.48	4.18	4.39	1.72	12.88	19.35
2	56.25	7.1	0.22	0.71	13.93	21.28
3	58.19	0.41	3.14	0.35	14.00	23.91
4	56.30	7.85	0.00	0.65	14.24	20.96
5	56.95	6.43	0.13	0.34	14.25	21.90
6	57.41	1.18	2.55	0.37	14.58	23.92
7	55.33	6.64	0.24	0.55	14.75	22.49
8	57.05	7.59	0.00	0.44	14.12	20.80
9	56.45	0.59	3.08	0.33	14.68	24.87
10	55.97	7.44	0.00	0.56	14.48	21.54
11	47.26	0.41	33.79	17.64	0.11	0.79
12	57.09	0.00	3.24	0.36	14.33	24.98

**Fig. 2.** SAED patterns of $\text{Cd}_{0.8}\text{Ba}_2(\text{Y}_{0.7}\text{Ca}_{0.4})\text{Cu}_{3.5}\text{O}_y$ (a) — for the $[331]$ zone axis and (b) — for the $[12\bar{1}]$ zone axis**Table 2.** Result of the elemental TEM-EDX analysis for crystals with $[331]$, $[12\bar{1}]$, $[001]$ and $[010]$ orientations

Element/line	at% $[331]$	at% $[12\bar{1}]$	at% $[001]$	at% $[010]$
Cu-K	16.3	17.9	30.0	21.9
Ba-L	11.7	12.0	17.3	14.8
Y-K	4.3	4.6	6.7	5.8
Cd-L	0.4	0.6	1.6	0
Ca-K	0.9	1.0	3.4	0.5
O-K	66.4	63.9	41.0	57

Investigation along the $[001]$ and $[010]$ zones was also performed. It may be seen in the figure that the SAED pattern of the $[331]$ zone has a single-phase character. The SAED pattern of $[12\bar{1}]$ has a great single-crystal character with diffuse maxima. The results of the elemental EDX analysis are given in Table 2. If we assume a full occupancy of the Cu-sites with Cu^{2+} ions, the calculations showed chemical compositions of $(\text{Y}_{0.78}\text{Cd}_{0.07}\text{Ca}_{0.16})\text{Ba}_{2.15}\text{Cu}_3\text{O}_y$ and $(\text{Y}_{0.77}\text{Cd}_{0.08}\text{Ca}_{0.16})\text{Ba}_{2.01}\text{Cu}_3\text{O}_y$ for the areas with $[331]$ and $[12\bar{1}]$ orientations respectively. Another area with $[331]$ orientation gives nearly the same cationic content — $(\text{Y}_{0.76}\text{Cd}_{0.09}\text{Ca}_{0.16})\text{Ba}_{2.15}\text{Cu}_3\text{O}_y$. From the

data of the Table 2 it may be concluded that Cd and Ca enter the 123 phase in the microcrystals with [331], [121] and [001] orientations. However the distribution of the two elements along the different single crystals is inhomogeneous and Cd is not present in the crystals with [010] orientation. Further investigations for determination of the Cd and Ca positions in the lattice structure are in progress.

The susceptibility measurements of the $\text{Cd}_{0.8}\text{Ba}_2(\text{Y}_{0.7}\text{Ca}_{0.4})\text{Cu}_{3.5}\text{O}_y$ samples showed a $T_c = 80$ K and a superconducting volume fraction of 33% [9]. If we assume the presence of an undoped 123 with lattice parameters, changed only by the oxygen content, the sample would have a diamagnetic value of $T_c = 90$ K [10]. If we also assume the presence of an intergrowth of CdO with only Ca-doped 123, the resulting product would still have a diamagnetic transition temperature of 90–92 K [6].

3. Conclusion

We synthesized and investigated a new Cd and Ca-containing superconductor with $T_c = 80$ K and nominal composition $\text{Cd}_{0.8}\text{Ba}_2(\text{Y}_{0.7}\text{Ca}_{0.4})\text{Cu}_{3.5}\text{O}_y$. The dominating phase was identified as an orthorhombic 123. It was shown that the Cd and Ca doping facilitates the 123 phase formation. The results of the SEM and TEM investigations showed that the investigated samples are inhomogeneous. The two elements are present in most of the investigated crystals and form a new Cd-Ba-Y-Ca-Cu-O superconductor.

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