x=0.025 Co is shown in the inset of Fig.
perature range 160 – 250 K according to
of the carriers is most probably related to
magnetostrictively and Hall effect
doped with Co. The intergrain critical
field amplitude for x=0.00 and 0.025 Co
The Co ions induce the increase for α1
dependence of the electrical resistivity is
tual resistivity increases with x. The width
using magnetic field. The activation en-
y in x=0.025 Co sample, evidenced two
and lower temperature (I). The activation
β1 (regime I). In x=0.00 sample only the
lnB is present. In normal state the charge
contents in the samples. The anomalies on
are discussed in the framework of phase

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ATTEMPT OF IDENTIFICATION OF SUPERCONDUCTING PHASE (102 K)
IN CdBa2Ca_n-1Cu_nO_x SAMPLES

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Abstract

The samples of homologous series CdBa2Ca_n-
1Cu_nO_x+2y (n = 0, 1, 2, 3, 4), CdBaCaCuOx+y,
CdBaCa2CuOy-z, Cd2BaCaCuOy+z, and CdBaCuOy-z
were prepared by solid state reaction. The superconducting
transition in samples was found at 90–102 K. The
presence of diamagnetic phases was confirmed by
magnetic measurements. BaCuO2 and CaCdO2 were
identified as main phases. Superconductivity of samples
was associated with change of properties of
aforementioned phases as a result of Cd, Ba and Ca
doping.

Introduction

The special interest to Cd-containing ceramics was initiated after the discovery of
superconductivity at 133.5 K in Hg-Ba-Ca-Cu-O system. It was associated with volatility,
toxicity and difficult preparation technology of mercurium oxide. Cadmium is a candidate for
inclusion in this system as analogue of mercurium by chemical properties.

The similarity of the chemical properties and closeness of the ion radii of mercury and
cadmium may forecast the existence of homologous series CdBa2Ca_n-1Cu_nO_x+2y-z.

Experimental

Two series of samples of Cd-Ba-Ca-Cu-O ceramics were prepared by solid state
reaction. The samples of seria A were obtained in two steps. In first step the stoichiometric
mixtures of BaCO3, CaCO3 and CuO (all analytical pure) were fired at 930–950 °C for
24 hours for BaCaCuO oxide. In second step the obtained powders were reground with

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CdO in mortar and fired at 930 °C in oxygen for 24 hours too. The series B was prepared by heating of CdO, BaCO₃, CaCO₃ and CuO at 930 °C in oxygen for 24 hours. All samples were examined by X-ray powder diffraction analysis with CuKα-radiation on DRON-3 diffractometer. The temperature dependence of electroconductivity was investigated by standard four-probe method in region 4-300 K. Presence of superconducting phase was identified by magnetic measurements.

Results and discussion

Figure 1 shows the X-ray diffraction pattern of samples with nominal composition CdBa₂CaCu₂O₆±δ. The main peaks belong to the cubic binary oxides BaCuO₂ (space group Im3m, a = 18.28 Å) and CaCdO₂ (space group Fm3m, a = 4.760(5) Å).

Figure 1. XRD pattern of CdBa₂CaCu₂O₆±δ ceramics.

Balchev et al. [1] have reported about obtaining of original phase that was related to new Cd-based composition CdBa₂CaCu₂O₆±δ. This phase was identified by group of peaks in region 2θ = 25 ± 45 degree. Here we show that all found peaks belong to BaCuO₂ and CaCdO₂ phases only. This inaccurate interpretation, perhaps, is a result of limited data using [2]. Superconductivity of samples was associated with presence of CdBaCaCuO₆±δ, CdBaCa₂CuO₆±δ and Cd₂Ba₂Ca₂Cu₃O₆+δ phases. In this work we have synthesized the ceramics of this composition. It was founded that the samples are multiphase and are containing of BaCuO₂ and CaCdO₂ peaks observed despite the different cations' ratio associate it with mutual doping of Ca, O.

The next step of investigation was to synthesize series of samples with BaCuO₂ × 0.2CaCdO₂ and CuO × 0.2CaCdO₂ nominal composition. The temperature of superconducting transition, however, did not change much. We think that the superconducting phase is present in BaCuO₂. Jin C.-Q. et al. [3] have reported on samples of Ba-Ca-Cu-O system where it is possible that we observed some amount of this phase.

Interest to ceramics of CdBa₂CaCu₂O₆±δ is that superconducting samples with superconducting phase has an orthorhombic structure. This structure is not found in samples with CdBaCaCuO₆±δ nominal composition that can not be obtained at these conditions. BaCuO₂ and CdO (Figure 2).

Figure 2. XRD pattern of BaCuO₂ and CdO.
The seria B was prepared by a oxygen for 24 hours. All samples were

ultrasonic using CuKα-radiation on DRON-3 diffractometer. Conductivity was investigated by EPR measurement. Presence of superconducting phase was

assumed in samples with nominal composition of cubic binary oxides BaCuO₂ (space group \( a = 4.760(5) \text{ Å} \)).

The next step of investigation was the checking of superconductivity of samples with BaCuO₂ × 0.2CaCdO₂ and CaCdO₂ × 0.2BaCuO₂ nominal composition. These samples were synthesized by the same technology. It was found that the sample with BaCuO₂ × 0.2CaCdO₂ nominal composition has superconducting properties. The value of the temperature of superconducting transition of this sample is maximal (Table). For this reason we think that the superconducting phase have a crystal lattice based on cubic structure BaCuO₂. Jin C.-Q. et al. [3] have reported about strong diamagnetic signals at \( T_c = 117 \text{ K} \) for samples of Ba-Ca-Cu-O system which was associated with its superconductivity. It is possible that we observed some amounts of this phase.

Interest to ceramics of CdBa₂Cu₃O₈+δ composition was initiated by Balchev at al. [4] where superconducting samples with CdₓBa₃(Yₓ)Ca₄Cu₄Oₓ were observed. The superconducting phase has an orthorhombic cell (type YBa₂Cu₄O₈). We have synthesized the samples with CdBa₂Cu₃O₈+δ nominal composition. It was found that CdBa₂Cu₃O₈+δ phase can not be obtained at these conditions of synthesis. These samples are the mixture of BaCuO₂ and CdO (Figure 2).

![Figure 2. XRD pattern of CdBa₂Cu₃O₈+δ ceramics.](image)
The properties of the samples of Cd – Ba – Ca – Cu - O system are presented in Table.

<table>
<thead>
<tr>
<th>Number of sample</th>
<th>Nominal composition</th>
<th>T_c, K</th>
<th>Main phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>CdBa_2CaCu_2O_{6+x}</td>
<td>28 (102)</td>
<td>BaCuO_2, CaCdO_2</td>
</tr>
<tr>
<td>A2</td>
<td>CdBa_2CaCu_2O_{6+x}</td>
<td>25 (97)</td>
<td>BaCuO_2, CaCdO_2</td>
</tr>
<tr>
<td>A3</td>
<td>CdBa_2CaCu_2O_{6+x}</td>
<td>25 (90)</td>
<td>BaCuO_2, CaCdO_2</td>
</tr>
<tr>
<td>B1</td>
<td>CdBa_2CuO_4±8</td>
<td>40</td>
<td>BaCuO_2, CdO</td>
</tr>
<tr>
<td>B2</td>
<td>CdBa_2CaCuO_3±8</td>
<td>35</td>
<td>BaCuO_2, CaCdO_2</td>
</tr>
<tr>
<td>B3</td>
<td>CdBa_2CaCuO_3±8</td>
<td>25</td>
<td>BaCuO_2, CaCdO_2</td>
</tr>
<tr>
<td>B4</td>
<td>CdBa_2CaCuO_3±8</td>
<td>38</td>
<td>BaCuO_2, CaCdO_2</td>
</tr>
<tr>
<td>B5</td>
<td>CdBa_2CaCuO_3±8</td>
<td>non-supercond.</td>
<td>BaCuO_2, CuO, CdO</td>
</tr>
<tr>
<td>B6</td>
<td>CdBa_2CaCuO_3±8</td>
<td>non-supercond.</td>
<td>BaCuO_2, CuO, CdO</td>
</tr>
<tr>
<td>B7</td>
<td>CdBa_2CuO_4±8</td>
<td>25</td>
<td>BaCuO_2, CdO</td>
</tr>
<tr>
<td>B8</td>
<td>Cd_2BaCu_2O_4±8</td>
<td>41</td>
<td>BaCuO_2</td>
</tr>
<tr>
<td>B9</td>
<td>CdBa_2CaCuO_3±8</td>
<td>non-supercond.</td>
<td>CaCdO_2</td>
</tr>
</tbody>
</table>

The presence of diamagnetic phases was confirmed by magnetic measurements. Probably the superconductivity of samples is caused by one superconducting phase.

In summary, this work is an attempt of identification of superconducting phase in system Cd-Ba-Ca-Cu-O system. The samples with CdBa_2CuO_{4+δ}, CdBa_2CaCuO_{6+δ}, CdBa_2Ca_2Cu_2O_{4+δ}, CdBa_2CaCuO_{4+δ}, CdBa_2CaCuO_{3+δ}, CdBa_2CaCuO_{3+δ}, CdBa_2CaCuO_{1+δ}, CdBa_2CuO_{5+δ}, CdBa_2CaCuO_{1+δ}, CdBa_2CuO_{1+δ}, CdBa_2CuO_{1+δ} nominal composition were prepared by solid state reaction. It was founded that superconducting properties of samples are caused by Cd-doped BaCuO_2 phase.

References