SUPERCONDUCTIVITY AT 100 K IN Cd-Ba-Ca-Cu-O CERAMICS

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The samples of a homologous series $CdBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ (n = 0, 1, 2, 3, 4), $CdBaCaCuO_{4+\delta}$, $CdBaCa_2CuO_{5+\delta}$, $Cd_2Ba_3Ca_3Cu_3O_{11+\delta}$ and $CdBa_2Cu_3O_{6+\delta}$ were prepared by solid state reaction. The superconducting transition in the samples was found at 90÷102 K. The presence of diamagnetic phases was confirmed by magnetic measurements. $BaCuO_2$ and $CaCdO_2$ were identified as main phases. Superconductivity of the samples is associated with the formation of Cd-doped $BaCuO_2$ phase.

Introduction

The group of $HgBa_2Ca_{n-1}Cu_nO_x$ with crossover temperatures 94 K (n=1), 123 K (n=2), and 133 K (n=3) was the last explored class of $ABa_2Ca_{n-1}Cu_nO_x$ HTSC homologous lines (A= Bi, Tl, Hg, n=1,2,3...) [1]. This was associated with volatility, toxicity and difficult preparation technology of mercuric oxide. Cadmium is a candidate for inclusion in such system as an analogue of mercury by chemical properties.

The similarity of chemical properties and closeness of the ion radii of mercury and cadmium initiate the task of investigating the existence of $CdBa_2Ca_{n-1}Cu_nO_{2+2n+\delta}$ homologous series. The attempts to make $CdBa_2CaCu_2O_{6+\delta}$ and $CdBa_2Ca_2Cu_3O_{8+\delta}$ samples were described in [2] and [3], accordingly. The multiphase samples were obtained and T_c = 107 K was reported. Superconductivity was associated with $CdBaCaCuO_{4+\delta}$, $CdBaCa_2CuO_{5+\delta}$ and $Cd_2Ba_3Ca_3Cu_3O_{11+\delta}$ phases. The sample of $Cd_{0.8}Ba_2(Y_{0.7}Ca_{0.4})Cu_{3.5}O_y$ with T_c = 80 K was synthesized in [4]. It was reported that the main phase is orthorhombic ($YBa_2Cu_3O_7$-type).

Experimental

Two series of samples of Cd-Ba-Ca-Cu-O ceramics were prepared by solid state reaction. The samples of series A were obtained by two step technique. At the first step the stoichiometric mixtures of $BaCO_3$, $CaCO_3$ and CuO (all analytical pure) were fired at 930 ÷ 950 °C for 24 hours for $Ba_xCa_yCu_zO_t$ oxide. At the second step the obtained powders were reground with CdO in a mortar and were fired at 930 °C in oxygen for another 24 hours. Series B was prepared by heating CdO, $BaCO_3$, $CaCO_3$ and CuO at 930 °C in oxygen for 24 hours.

The X-ray powder diffraction (XRD) analysis was carried out on DRON-3 diffractometer with CuK_α-radiation. Temperature dependence of electric conductivity was investigated by standard four-probe method in the range 4–300 K. The presence of the superconducting phase was identified by magnetic measurements.

Results and discussion

It was reported that the samples of $CdBa_2CaCu_2O_{6+\delta}$ and $CdBa_2Ca_2Cu_3O_{8+\delta}$ nominal compositions are mixtures of non-superconducting binary oxides $BaCuO_2$ (space group *Im3m*, a = 18.28 Å) and

$CaCdO_2$ (space group *Fm3m*, a = 4.760(5) Å) [5, 6]. However, the superconducting properties of the above mentioned samples were discovered by electric and magnetic measurements (Table 1). The samples of $CdBa_2CaCu_2O_{6+\delta}$ and $CdBa_2Ca_2Cu_3O_{8+\delta}$ have shown diamagnetic properties at 28 and 25 K, respectively. The substantial width of the phase transition can be explained by low concentration of superconducting phase [5].

Table 1. The properties of the samples of Cd–Ba–Ca–Cu-O system.

Sample	Ratio				T_c, K
	Cd	Ba	Ca	Cu	
A1	1	2	1	2	28 (102)
A2	1	2	2	3	25 (97)
B1	1	2	-	1	40
B2	1	2	1	2	35
B3	1	2	2	3	25
B4	1	2	-	3	25
B5	0.2	1	0.2	1	41
B6	1	0.2	1	0.2	n.s.*

*n.s. – non-superconducting

The results of XRD analysis indicate that the superconducting phase has the structure of one of the oxides ($BaCuO_2$ or $CaCdO_2$). Therefore, the superconductivity of the samples with $BaCuO_2 \times 0.2CaCdO_2$ and $CaCdO_2 \times 0.2BaCuO_2$ nominal composition was investigated. These samples were synthesized by the same technology. It was found that only the sample with $BaCuO_2 \times 0.2CaCdO_2$ nominal composition has superconducting properties (Table 1). The maximum of T_c was found for $BaCuO_2$ sample with small $CaCdO_2$ addition.

Ba-Ca-Cu-O system was investigated in [7]. It was reported that the samples have superconducting properties after high-pressure oxygen treatment only. That is why we investigate the samples of Cd-Ba-Cu-O system.

We have synthesised the samples with $CdBa_2Cu_3O_{6+\delta}$ nominal composition. Figure 1 shows the X-ray diffraction pattern of samples with nominal composition $CdBa_2Cu_3O_{6+\delta}$. The main peaks belong to $BaCuO_2$ (indicated by Miller indices). CdO and CuO phases were determined as admixtures. The formation of $CdBa_2Cu_3O_{6+\delta}$ phase at these conditions of synthesis was not confirmed.

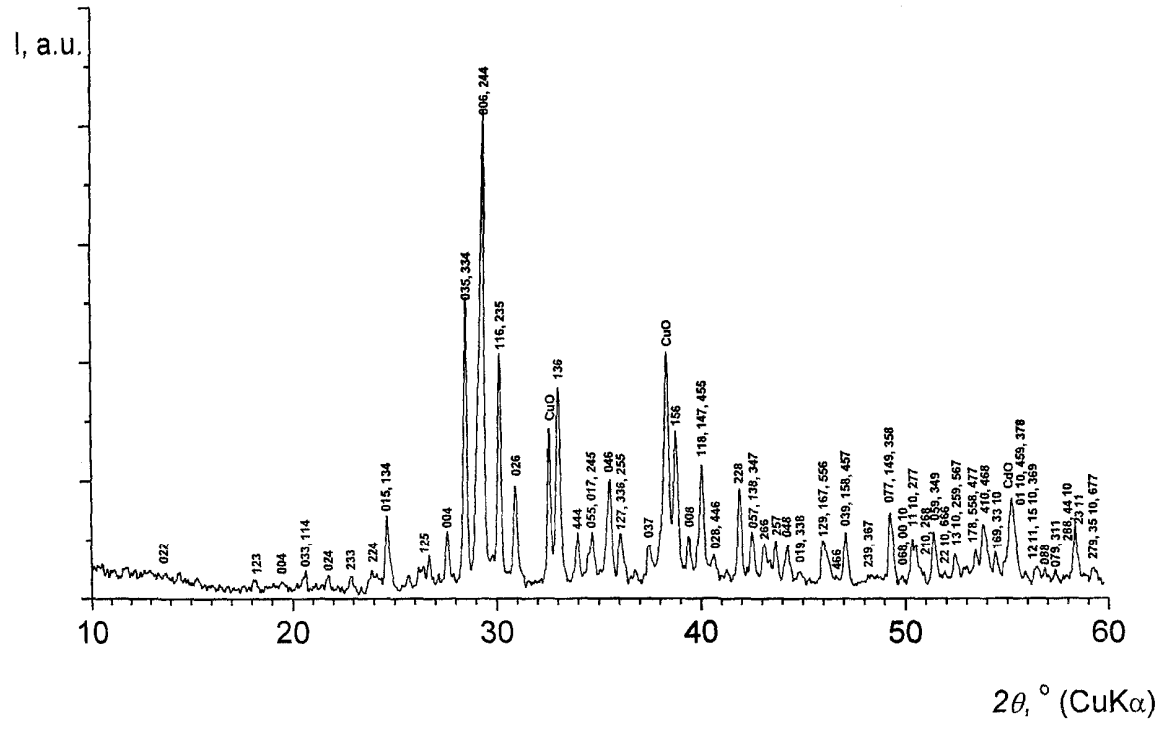

Fig. 1. XRD pattern of $CdBa_2Cu_3O_{6+\delta}$ ceramics.

The XRD analysis has shown the presence of well-known non-superconducting phases only. The results of magnetic measurements are different because the diamagnetic properties were found at 25 K. We attribute the presence of superconducting properties in the samples to the formation of Cd-doped $BaCuO_2$ phase.

Conclusion

In summary, this work is an attempt of identification of superconducting phase in Cd-Ba-Ca-Cu-O system. The samples with nominal composition $CdBa_2CaCu_2O_{6+\delta}$, $CdBa_2Ca_2Cu_3O_{8+\delta}$, $CdBa_2Cu_3O_{6+\delta}$, $CdBa_{0.2}CaCu_{0.2}O_x$, $Cd_{0.2}BaCa_{0.2}CuO_x$ were prepared by solid state reaction. On the base of the results of XRD analysis, electric and magnetic measurements the superconducting properties of samples were found to be caused by Cd-doped $BaCuO_2$ phase.

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НАДПРОВІДНІСТЬ ПРИ 100 К У КЕРАМІЦІ Cd-Ba-Ca-Cu-O

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Методом твердотільних реакцій приготовано зразки гомологічного ряду $CdBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ (n = 0, 1, 2, 3, 4), $CdBaCaCuO_{4+\delta}$, $CdBaCa_2CuO_{5+\delta}$, $Cd_2Ba_3Ca_3Cu_3O_{11+\delta}$ і $CdBa_2Cu_3O_{6+\delta}$. При 90÷102 К у зразках виявлено перехід у надпровідний стан. Наявність діамагнітних фаз підтверджено магнітними вимірюваннями. $BaCuO_2$ і $CaCdO_2$ ідентифіковано як головні фази. Надпровідність зразків пов'язується з утворенням легованої кадмієм фази $BaCuO_2$.