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Synthesis and characterization of $HgBa_2RCu_2O_{6+\delta}$ (R = Eu, Gd, Ho, Er, Tm, Yb and Y)

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Abstract

Compounds with the general formula $HgBa_2RCu_2O_{6+\delta}$ (Hg-1212 phase, R = Eu, Gd, Ho, Er, Tm, Yb and Y) were synthesized by solid state reaction. The influence of synthesis conditions on the phase composition of these samples was investigated.

X-ray powder and electron diffraction data have shown that all synthesized compounds are isostructural with the Hg-1212 phases containing rare earth elements of larger ionic radius, already published in literature. Different thermal annealings performed on the samples showed the impossibility of substantially changing the oxygen content of the synthesized compounds. Measurements of the temperature dependence of the magnetic susceptibility showed no diamagnetic signal down to 12 K.

Keywords: $HgBa_2RCu_2O_{6+\delta}$ compounds; Synthesis; Crystal structure

1. Introduction

The Hg-containing complex copper oxides are the subject of considerable interest since superconductivity with high T_c values was found for members of the $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ ($n = 1$–6) homologous series [1–6]. The $HgBa_2RCu_2O_{6+\delta}$ (R = rare earth element) compounds were first synthesized by Putilin et al. [7]. In contrast to the isostructural $HgBa_2CaCu_2O_{6+\delta}$ compound, these phases do not exhibit superconductivity. The formation of these compounds is very sensitive to the synthesis conditions due to the existence of a large number of compounds in the Hg–Ba–R–Cu–O system, some of which, like R_2BaCuO_5, are thermodynamically very stable [8]. This may be the reason why $HgBa_2RCu_2O_{6+\delta}$ phases, containing smaller rare earth elements than Sm, have not been obtained in single phase form. The values of the unit cell parameters of $HgBa_2RCu_2O_{6+\delta}$ phases decrease uniformly with decreasing rare earth ionic radius [7], providing a reduction of the in-plane Cu–O bond lengths in the (CuO_2) layers which are responsible for superconductivity. For small rare earth elements these distances are expected to be in the range of the typical values for high-T_c superconductors, while for the larger ones the Cu–O bond lengths are significantly larger than those found for hole-doped superconducting Cu mixed oxides. Therefore, we may expect superconductivity in the Hg-1212 compounds containing rare earth elements with smaller ionic radius.

The goal of this work was to synthesize and characterize $HgBa_2RCu_2O_{6+\delta}$ with R = Eu, Gd, Ho–Lu and Y.

2. Experimental

The samples were synthesized from the appropriate rare earth oxide, HgO, $Ba(NO_3)_2$ and CuO using the following procedure. First, R_2O_3 (R = Eu, Gd, Ho–Lu and Y), $Ba(NO_3)_2$ and CuO were mixed in an agate mortar and heated at 500°C under dynamic vacuum. Barium nitrate was chosen as a reactant since the synthesis with barium carbonate can lead to a stoi-

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chiometry deviation due to incomplete removal of the CO_2 from the annealed precursor. The stoichiometric amount of yellow HgO was added in a dry box filled with nitrogen and the sample was placed into an evacuated silica tube (oxygen pressure 10^{-3} Torr). The following annealing conditions were used: (1) 650°C, 50 h; (2) 650°C, 75 h; (3) 650°C, 100 h; (4) 750°C, 50 h; (5) 810°C, 60 h.

In order to increase the homogeneity of the precursor the weighed amounts of the appropriate rare earth oxide (Lu_2O_3 or Y_2O_3), CuO and $Ba(NO_3)_2$ were dissolved in nitric acid (40 wt.%), after which the solution was slowly evaporated and the precursor thus obtained was used in the subsequent synthesis.

Some of the samples were subjected to different thermal annealings. The Eu-containing sample was annealed in nitrogen flow at 300°C for 10 h. The Eu- and Gd-containing samples were annealed in oxygen flow at 300°C for 10 h. The Eu, Gd and Yb-containing samples were annealed at $P(O_2) = 100$ bar and 250°C for 10 h.

The phase composition of the synthesized samples was determined from X-ray powder data (Guinier focusing camera, Cu $K\alpha_1$ radiation, $\lambda = 1.54056$ Å; finely powdered germanium ($a = 5.65074$ Å) was used as an internal standard).

Crystallites of the Ho-containing sample were studied in a transmission electron microscope (Philips EM-430ST) with an accelerating voltage of 200 kV.

The oxygen stoichiometry of the Eu- and Gd-containing compounds was determined by iodometric titration [9].

The measurements of the magnetic susceptibility were carried out down to 12 K in a calibrated a.c.-susceptometer at 1 Oe and 74 Hz for the samples with R = Y and Yb.

3. Results and discussion

The $HgBa_2RCu_2O_{6+\delta}$ compounds were synthesized for R = Eu, Gd, Ho, Er, Tm, Yb and Y. Their unit cell parameters are given in Table 1. Phases with R = Ho, Er, Tm and Yb had not been previously synthesized and this series now embraces almost all rare earth elements. The Lu-containing phase was not formed under the present synthesis conditions; the probable reason for this is that the ionic radius of Lu is the lowest among the rare earth elements.

All samples were found to be multiphase, the content of the Hg-1212 phase ranging from 60 to 90%, depending on the rare earth element and synthesis conditions. The best results were obtained using synthesis conditions described in (3), i.e.650°C, 100 h. The content of the Hg-1212 compound in the prepared samples, from X-ray powder data, was found to be greatest for the Eu-containing sample (more than 95%).

From the X-ray powder data, all synthesized compounds were found to be isostructural and have tetragonal symmetry with tripling of the perovskite subcell along the c-axis. The unit cell parameters values were confirmed by electron diffraction. The electron diffraction patterns of $HgBa_2HoCu_2O_{6+\delta}$ taken along ⟨100⟩, ⟨110⟩ and [001] zone axes are shown in Fig. 1. No additional spots which could be attributed to the superstructure or satellite reflections were detected. Both unit cell parameters of

Table 1
Unit cell parameters of the $HgBa_2RCu_2O_{6+\delta}$ compounds

Formula	Appealing conditions	a (Å)	c (Å)	V (Å^3)
$HgBa_2EuCu_2O_{6+\delta}$	as-prepared	3.8925(5)	12.568(3)	190.4(1)
	nitrogen flow	3.8924(4)	12.563(7)	190.3(1)
	oxygen flow	3.8922(9)	12.583(5)	190.6(2)
	$P(O_2) = 100$ bar	3.8928(5)	12.583(5)	190.6(1)
$HgBa_2GdCu_2O_{6+\delta}$	as-prepared	3.8929(8)	12.548(5)	190.2(2)
	oxygen flow	3.8917(8)	12,543(3)	190.0(2)
	$P(O_2) = 100$ bar	3.8939(9)	12.552(4)	190.3(1)
$HgBa_2HoCu_2O_{6+\delta}$	as-prepared	3.8775(8)	12.522(5)	188.3(2)
$HgBa_2ErCu_2O_{6+\delta}$	as-prepared	3.8690(2)	12.493(9)	187.0(2)
$HgBa_2TmCu_2O_{6+\delta}$	as-prepared	3.8627(8)	12.481(7)	186.2(2)
$HgBa_2YbCu_2O_{6+\delta}$	as-prepared	3.8566(8)	12.478(6)	185.6(2)
	$P(O_2) = 100$ bar	3.857(2)	12.487(7)	185.8(3)
$HgBa_2YCu_2O_{6+\delta}$	as-prepared	3.8700(9)	12.515(4)	187.4(1)

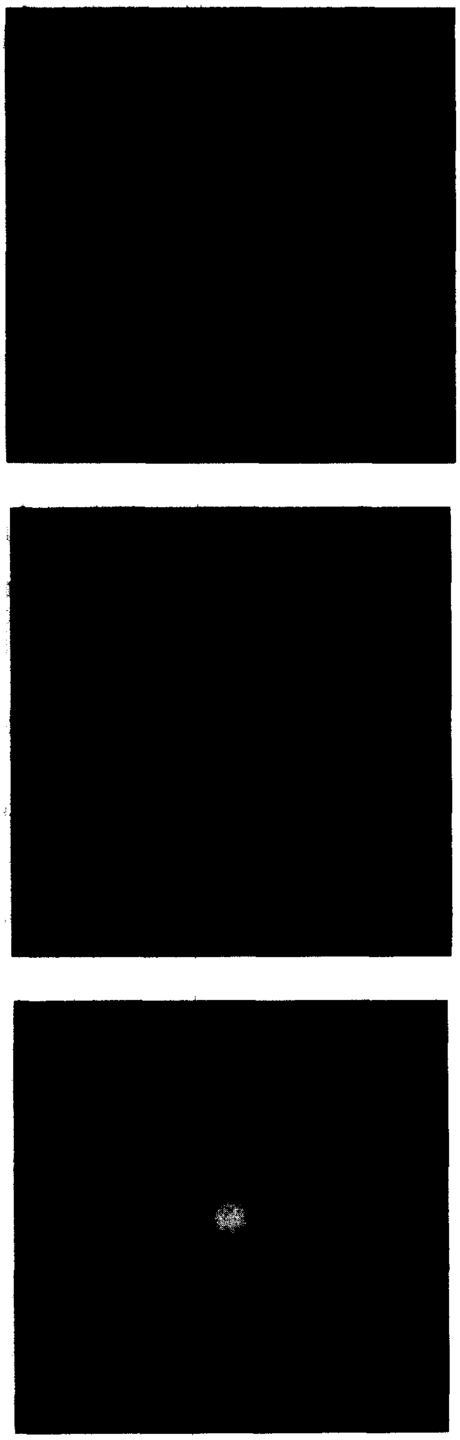

Fig. 1. Electron diffraction patterns of $HgBa_2HoCu_2O_{6+\delta}$ taken along (a) ⟨100⟩, (b) ⟨110⟩ and (c) [001] zone axes.

$HgBa_2RCu_2O_{6+\delta}$ decrease gradually with decreasing rare earth ionic radius (see Table 1).

Different phases were detected as impurities and their ratio was found to depend greatly on the synthesis conditions and the nature of the rare earth element. The impurities in the samples containing R = Ho, Er, Tm, Yb and Y were R_2BaCuO_5, CuO, $BaCuO_2$ and R_2O_3. These four compounds were also detected in the Lu-containing sample where the Hg-1212 phase was not formed. The impurities in the Eu- and Gd-containing samples were found to be different from the other samples, since R_2HgO_4 [10] appeared. However, the total amount of impurities in Eu- and Gd-containing samples was less than 5%. CuO and R_2O_3 were present in samples prepared at 650°C at lower synthesis times, which indicated an incomplete reaction. The increase of synthesis time up to 100 h led to a drastic decrease in the amount of these impurities. Nevertheless, we could not obtain monophasic Hg-1212 compounds for R = Ho, Er, Tm, Yb and Y, even after long annealing times. The reason for this may be a significant deviation of the phase composition from the ideal $HgBa_2RCu_2O_{6+\delta}$ stoichiometry, as was shown for the Sm-containing compound in Ref. [11], which can be even more pronounced for the smaller rare earth elements.

In comparison with Hg-1212 phases containing rare earth elements with larger ionic radius, the conditions for the preparation of these phases with smaller rare earth elements should be shifted to lower temperatures to avoid the formation of the thermodynamically very stable R_2BaCuO_5 phase. The content of R_2BaCuO_5 increases significantly with decreasing rare earth ionic radius and after synthesis at higher temperatures (750 or 810°C). In the Yb-containing sample we detected $HgBa_2CuO_{4+\delta}$ (Hg-1201 phase) as an impurity (about 40%). The reflections of this compound were indexed in the tetragonal symmetry with lattice parameters $a = 3.885(1)$ Å, $c = 9.542(4)$ Å.

The samples which were obtained using the evaporation of nitric solutions were found to contain much larger amounts and different types of impurity than those obtained using the usual procedure (the content of Hg-1212 phase did not exceed 20%). For example, $BaHgO_2$ [12] was detected, the formation of which can be explained by the vigorous character of decomposition of copper nitrate; this can lead to a deviation of the cation stoichiometry of the mixture.

The $\chi(T)$ measurements for Y- and Yb-containing samples showed no noticeable diamagnetic signal that might be attributed to the Hg-1212 phase down to 12 K. The superconducting transition with $T_{c,\ onset} = 93$ K, which was attributed to the Hg-1201 phase, was found for the Yb-containing sample. In contrast to Hg-1201 and the Ca-containing Hg-1212 phases, the rare-earth-containing Hg-1212 phase unit cell parameters were found not to change significantly after annealing in oxygen and nitrogen flows or under oxygen pressure ($P(O_2) = 100$ bar, see Table 1). The fact that oxygen treatment did not cause any substantial changes of the unit cell parameters may be an indication that these compounds have a fixed oxygen stoichiometry ($\delta \cong 0.5$). The iodometric titration of the as-prepared and oxygen-treated $HgBa_2EuCu_2O_{6+\delta}$

and $HgBa_2GdCu_2O_{6+\delta}$ samples showed no noticeable differences of the formal copper valence, which was always close to +2. This is a significant difference compared with Ca-containing Hg-1212 phases, for which the δ-value can be varied within a broad range by different thermal annealings [13,14]. Therefore, the absence of superconductivity in rare-earth-containing Hg-1212 phases can be explained in terms of insufficient hole concentration in the conductivity band, the increase of which cannot be achieved by thermal annealings even at high oxygen pressure. Thus, one possible way to induce superconductivity in these compounds is to use heterovalent replacement of trivalent rare earth cations by divalent Ca cations, as has been shown for Sm-, Dy-, Nd- and Y-containing Hg-1212 phases [11,15–17]. No results concerning solid solutions with the $HgBa_2R_{1-x}Ca_xCu_2O_{6+\delta}$ (R = Eu, Gd, Ho, Er, Tm, Yb) composition have yet been obtained. We consider that further studies of these systems are required for a better understanding of this problem.

4. Conclusions

Hg-1212 phases containing a wide variety of different rare earth elements were synthesized. Those containing Ho, Er, Tm and Yb were synthesized for the first time. X-ray powder and electron diffraction studies have shown that all synthesized compounds are isostructural with the Hg-1212 phases containing rare earth elements with larger ionic radius. Thermal annealing of the samples at various conditions showed that, in contrast to Ca-containing Hg-1212, it is not possible for these phases to change their oxygen stoichiometry and to increase their carrier concentration in the conductivity band. This may be the reason for the absence of superconducting properties in these phases.

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