Journal of Alloys and Compounds, 191 (1993) 297–300
JALCOM 515

The Yb_2O_3–CuO system and the crystal structure of $Yb_2Cu_2O_5$

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(Received May 20, 1992; in final form September 9, 1992)

Abstract

The phase diagram of the Yb_2O_3–CuO binary system was investigated by means of X-ray diffraction and thermal analysis. Under the present synthesising conditions, only one compound, $Yb_2Cu_2O_5$, was identified in this system. It is isostructural to $Y_2Cu_2O_5$ and its atomic parameters were refined using the Rietveld method. Specific heat measurements indicated that $Yb_2Cu_2O_5$ is quite stable in the temperature range between −150 and 800 °C; no structural transition was found in this temperature range.

1. Introduction

Up to now, a series of R_2O_3–CuO (R, rare earth) binary systems have been investigated to search for superconductors and clarify the phase relation for crystal growth since the discovery of superconductivity in the La_2O_3–CuO system [1–5]. The results show that there only exists one compound in each system when synthesized in air and that these belong to at least four types of crystal structure with decreasing ionic radius of rare earth: (1) La_2CuO_4 type (*Bmab*; T phase; ambient temperature); (2) Nd_2CuO_4 type (*I4/mmm*; T′ phase; R≡Nd, Pr, Sm, Eu, Gd); (3) $(R,R')_2CuO_4$ (*P4/nmm*; T* phase; R and R′, early and later rare earths respectively); (4) $Y_2Cu_2O_5$ type ($Pna2_1$; R≡Y, Ho, etc.). This means that a crystallographic evolution exists in the R_2CuO_4 compounds with decreasing ionic radius of rare earth, and if this ionic radius is small enough, a $Y_2Cu_2O_5$-type compound will form instead of any R_2CuO_4-type compound. R_2CuO_4 can be made superconducting by doping with oxygen or alkaline earths, Ce, etc. However, no $R_2Cu_2O_5$-type compound has been reported to be superconducting. As part of a series of studies, in this paper we report the phase relation of the Yb_2O_3–CuO binary system and the crystal structure and specific heat of $Yb_2Cu_2O_5$.

2. Experimental details

A series of Yb_2O_3–CuO samples with different compositions were prepared by solid state reaction of appropriate mixtures of high purity Yb_2O_3 and CuO. The powders were mixed, ground and fired at 950 °C for 12 h in air. Three additional firings for 24 h intervals with intermediate grindings were performed before the samples were pressed into pellets with a diameter of 10–12 mm and a thickness of 2–4 mm. The pellets were then sintered at 980 °C for 5 days.

Phase identifications were performed on a Guinier–De Wolff monochromatic-focusing transmission camera. High purity Si was added to the samples as an internal standard to correct the 2θ position of diffraction peaks. Structure refinement data were collected in a Rigaku automatic diffractometer using Cu Kα radiation with a graphite monochromator at room temperature. The scanning step is 0.02° and the scanning time is 5 s per step.

The melting points for all samples were measured using a home-made differential thermal analysis (DTA) apparatus with a Pt–PtRh thermocouple; Al_2O_3 was used as the reference sample. The heating and cooling rates were 10 °C min^{-1}. The specific heat was measured with an adiabatic scanning calorimeter (Ulvac Sinku Riko Model SH-3000, Japan) at a heating rate of 2 °C min^{-1}.

3. Results and discussion

3.1. Phase relation of Yb_2O_3–CuO

Thirteen samples of $(Yb_2O_3)_x(CuO)_{1-x}$ were prepared with compositions x=0.1, 0.15, 0.2, 0.25, 0.3, 0.33, 0.35,

0925-8388/93/$6.00

0.4, 0.45, 0.5, 0.55, 0.6 and 0.65. Samples with $x > 0.65$ were not prepared, since the melting point of Yb_2O_3 is quite high and the DTA apparatus working limit is below 1300 °C. Figure 1 shows the phase relation of this system, where the liquidus beyond $x = 0.65$ was not measured but is tentatively extrapolated as the broken curve. It can be seen that under the present sintering conditions only one compound, $Yb_2Cu_2O_5$, was formed; no other compounds were identified. Under the experimental conditions $Yb_2Cu_2O_5$ is an incongruent compound resulting from a peritectic reaction between liquid (L) and Yb_2O_3. The peritectic temperature is 1103 ± 10 °C. CuO also reacts eutectically with $Yb_2Cu_2O_5$ at about 1090 ± 10 °C to give an approximate eutectic composition of 31–32 mol% Yb_2O_3.

Since the compositional and temperature ranges for $L + Yb_2Cu_2O_5$ are quite narrow, appropriate flux, *e.g.* KF, is needed to grow good single crystals of $Yb_2Cu_2O_5$.

3.2. *Crystal structure of $Yb_2Cu_2O_5$*

The compound exhibits a light green colour. Its X-ray powder diffraction pattern indicates that it belongs to an orthorhombic system with cell parameters $a = 10.724$ Å, $b = 4.433$ Å and $c = 12.349$ Å, which is nearly identical to Lambert and Eysel's results [6]. According to the systematic extinctions $k + l = 2n + 1$ for $0kl$, $h = 2n + 1$ for $h0l$, $h = 2n + 1$ for $h00$, $k = 2n + 1$ for $0k0$ and $l = 2n + 1$ for $00l$, the possible space groups are $Pna2_1$ and $Pnam$. Freund and Buschbaum proposed that it is isostructural with $Ho_2Cu_2O_5$ [6, 7] and has space group $Pna2_1$, but its atomic position in the unit cell has not been determined. For this reason we collected diffraction data ranging from $2\theta = 12°$ to 70° using a step-scanning technique and utilized the Rietveld method to determine the atomic parameters and the thermal parameter which are listed in Table 1. Figure 2 shows the Rietveld refinement patterns. Table 2 gives

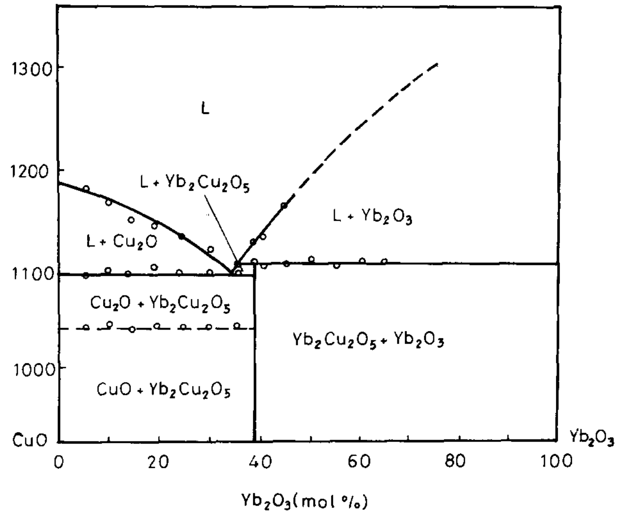

Fig. 1. Pseudobinary phase diagram of Yb_2O_3–CuO: circles, experimental results, horizontal broken line, decomposition of CuO at 1025 °C.

TABLE 1. Atomic parameters x, y, z, B and N for $Yb_2Cu_2O_5$; $Pna2_1$, $a = 10.724$ Å, $b = 4.433$ Å, $c = 12.319$ Å

Atom	x	y	z	B (Å^2)	N
Yb1	0.2078	0.2418	0.5397	1.50	4.0
Yb2	0.0301	0.2299	0.8688	0.01	4.0
Cu1	0.9945	0.6408	0.6466	2.64	4.0
Cu2	0.2634	0.6602	0.7511	0.35	4.0
O1	0.2006	0.7211	0.8897	0.19	4.0
O2	0.3411	0.7397	0.6113	0.44	4.0
O3	0.1112	0.1112	0.6993	0.37	4.0
O4	0.4307	0.7886	0.8123	1.66	4.0
O5	0.0998	0.3987	0.5052	0.05	4.0

$R = 0.085$, $R_{wp} = 0.122$

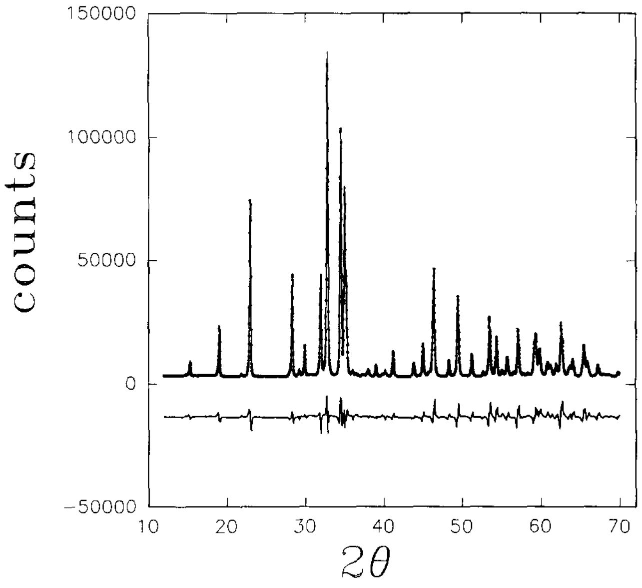

Fig. 2. Rietveld refinement profile of $Yb_2Cu_2O_5$ at room temperature: dots, raw data, solid curve, calculated profile. The curve at the bottom represents the difference between the observed and calculated profiles.

TABLE 2. Bond lengths (Å) between cations and oxygen

Yb1–O1	2.200	Yb2–O1	2.464
O2	2.374	O1	2.416
O2	2.374	O3	2.242
O3	2.258	O4	2.246
O5	1.992	O4	2.158
O5	2.309	O5	2.304
Cu1–O2	1.820	Cu2–O1	1.856
O3	2.569	O2	1.949
O4	2.127	O3	2.790
O5	1.818	O3	2.120
O5	2.197	O4	2.018

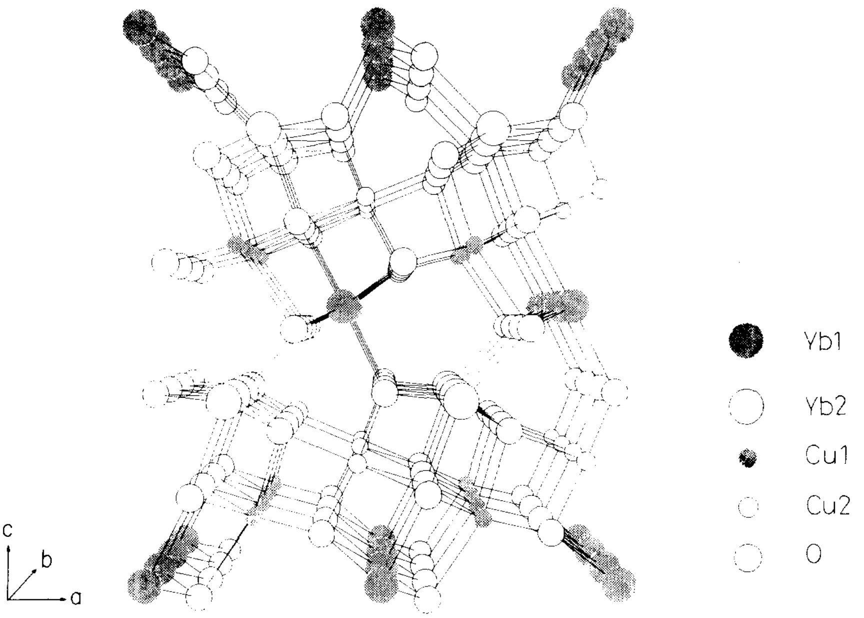

Fig. 3. Schematic view of crystal structure of $Yb_2Cu_2O_5$.

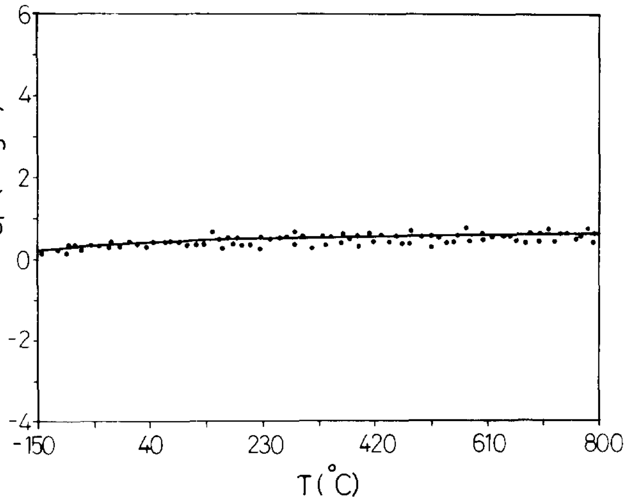

Fig. 4. Variation in C_p of $Yb_2Cu_2O_5$ vs. temperature; $C_p=0.241+0.5\times10^{-3}T-1.187\times10^{3}-2.4294\times10^{-7}T^{-2}$.

the bond lengths between cations and oxygen and Fig. 3 is a schematic perspective view of the $Yb_2Cu_2O_5$ crystal structure with the origin at Yb1 (0.2078, 0.2418, 0.5279). Every ion occupies a general site 4(*a*). Yb1 is coordinated with six oxygen atoms, namely O1 at 2.201 Å, two O2 at 2.374 Å, O3 at 2.258 Å and two O5 at 1.98 and 2.309 Å, giving an average Yb1–O distance of 2.249 Å, forming a distorted hexahedron. Like Yb1, Yb2 is also hexahedrally coordinated, with two O1 at 2.464 and 2.416 Å, O3 at 2.242 Å, two O4 at 2.264 and 2.158 Å and O5 at 2.304 Å, giving an average Yb2–O distance of 2.338 Å, slightly larger than the Yb1–O distance. The Cu–O coordinations are different from that for Yb–O. Each Cu is linked to five oxygen atoms. Cu1 has four nearest neighbours, namely O2, O4 and two O5 at 1.82, 2.127, 1.816 and 2.197 Å respectively, as well as a fifth, weakly bonded apical O3 at 2.569 Å. A similar distorted pyramidal coordination was observed for Cu2–O, with O1 at 1.856 Å, O2 at 1.949 Å, O3 at 2.120 Å, O4 at 2.018 Å and a fifth, weakly bonded apical O3 at 2.790 Å. The reason for the wide range of Cu–O bond lengths is not clear at present.

3.3. Specific heat of $Yb_2Cu_2O_5$

In order to investigate the phase stability of $Yb_2Cu_2O_5$ and obtain its specific heat data, we measured the specific heat of $Yb_2Cu_2O_5$ from 1073 K (800 °C) down to 117 K (−150 °C) in an adiabatic scanning calorimeter. The collected data were fitted to a polynomial by a least-squares reduction method, the adopted polynomial being $C_p=A+BT+CT^{-2}+DT^2$. Figure 4 shows the variation in C_p of $Yb_2Cu_2O_5$ *vs.* temperature. It can be seen that C_p increases slowly with increasing temperature; no peaks of a phase transition of first or second order were detected. This indicates that, unlike La_2CuO_4 which undergoes a displacive transition from a tetragonal form (*I4/mmm*) to an orthorhombic form (*Bmab*), $Yb_2Cu_2O_5$ is quite stable within the temperature range 117–1073 K.

Acknowledgment

This work is supported by the National Center for Development of Superconductivity.

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