

LETTER TO THE EDITOR

**X-RAY AND ELECTRON SPIN RESONANCE ON $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$
PREPARED BY CITRATE SYNTHESIS**

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Received 2 June 1987

$\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ samples were prepared by a citrate synthesis technique. Powder X-ray diffraction and resistance measurements were performed for sample characterization. This single-phase material has a T_c ($R=0$) of 91.2 K. Electron spin resonance experiments indicate the presence of 10 to 15% of Cu^{3+} .

1. Introduction

Since the discovery of superconducting properties of the La–Ba–Cu–O system at temperatures up to about 30 K [1] extensive research activities have been started on the exciting area of high T_c superconductors. Very high transition temperatures have been found in the $\text{M}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ series with for $\text{M}=\text{Y}$ a T_c -value of about 91 K [2]. Superconducting behaviour up to 240 K has been recently found in the Y–Ba–Cu–O system by observing the reverse ac Josephson effect [3].

In this letter we concentrate on $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ prepared by a citrate synthesis method which offers the possibility to start with grains with dimensions of some tens of nanometers. Each grain has already the desired ratios of the elements Y, Ba, Cu and O. Beside the citrate synthesis method we also prepared samples by solid state reactions starting from the oxides. Powder X-ray diffraction measurements will be shown and the 2θ -values and intensities of the relevant reflections will be compared with calculations. Resistance measurements exhibit an onset temperature of 99 K, whereas the sample becomes resistanceless at 91.2 K.

In order to study the valence of the Cu-ions in the compound we performed X- and Q-band electron spin resonance experiments. It is obvious that both Cu^{2+} and Cu^{3+} will appear in this

compound each having a characteristic energy splitting and line width dependent on the crystal field symmetry of the surrounding oxygen configuration.

2. Sample preparation

$\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ is often prepared by a series of solid state reactions starting with an appropriate mixture of the oxides Y_2O_3 , BaO (or BaCO_3) and CuO and by grinding between two consecutive reactions. It is not possible to obtain grains smaller than about $1\ \mu\text{m}$ and this hampers the solid state reaction. However, one may obtain good quality single-phase samples after a rather extensive procedure. We also used this technique and were able to prepare single-phase $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ with T_c -values above 90 K. Three solid state reactions were performed in air at 950°C and afterwards pressed pellets were sintered in oxygen flow at 950°C for 10 hours, finally slowly cooling down with $100^\circ\text{C}/\text{h}$.

As an alternative we prepared samples starting with a citrate synthesis technique. The Y_2O_3 , BaCO_3 and CuO were solved in nitric acid. After adding citric acid and neutralization with ammonia we got with pyrolyse an ultra fine and very homogeneous powder with typical size of about 60 nm. This powder was calcinated at

950°C for 10 hours in oxygen, pressed into pellets, sintered for 15 hours at 950°C and finally cooled down at a rate of 50°C/h in air.

3. X-ray diffraction

The effects of the various steps in the sample preparation were investigated by powder X-ray diffraction. We used a Debye–Scherrer diffractometer with Cu K_α source. The spectrum of the citrate synthesis powder after the solid state reaction including the calcination is presented in fig. 1 and it appears that the material consists of one phase $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ with only very small amounts of impurities. Some unreacted CuO can be seen at 2θ -values of 35.5°, and 48.8°. The two impurity reflections around 30° are very close to the two dominant lines of BaCuO_2 but do not coincide with these. We believe that these lines have to be attributed to Y_2BaCuO_5 . The impurity reflections were even smaller after the sintering process. It was found that the crystal growth and rearrangement show preferential orientations. Especially the (100) and (200) reflections become weaker while at the same time the (010) + (003) and (020) + (006) reflections increase in intensity.

In table I we present the major (hkl)-reflec-

Table I

Powder X-ray diffraction pattern for $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. Orthorhombic lattice parameters, $a = 3.82 \text{ \AA}$, $b = 3.89 \text{ \AA}$ and $c = 11.67 \text{ \AA}$, with d = distance between the scattering planes

hkl	$d(\text{\AA})$	2θ	I_{obs}	I_{Cava}	I_{calc}
001	11.670	7.57			5.4
002	5.835	15.17			3.7
003 + 010	3.890	22.84	11.9	11	13.3
100	3.820	23.27	3.6	3	4.1
012	3.237	27.53	3.3	3	3.1
102	3.196	27.89	4.8	5	5.5
013	2.751	32.52	47.6	60	46.3
110 + 103	2.726	32.83	100	100	100
111	2.654	33.74	1.2	2	1.0
112	2.469	36.36	2.1	3	2.1
014 + 005	2.334	38.54	13.7	11	7.4
104	2.319	38.80	3.0	3	1.6
113	2.232	40.38	13.4	13	11.3
020 + 006	1.945	46.67	22.9	23	16.8
200	1.910	47.57	8.9	10	10.0
115	1.773	51.50	3.8	3	2.0
023 + 016	1.740	52.55	1.8	2	1.3
120 + 106	1.733	52.78	1.2	2	1.0
203 + 210					
+ 121	1.714	53.41	1.2	2	1.3
122	1.662	55.22	2.1	1	0.8
123 + 116	1.583	58.23	28.0	24	19.2
213	1.569	58.80	10.4	11	9.0
025	1.494	62.07	2.1		1.2
205 + 214	1.478	62.82	2.4		1.8
026	1.375	68.14	3.6		2.4
220 + 206					
+ 108	1.363	68.82	11.3		6.2

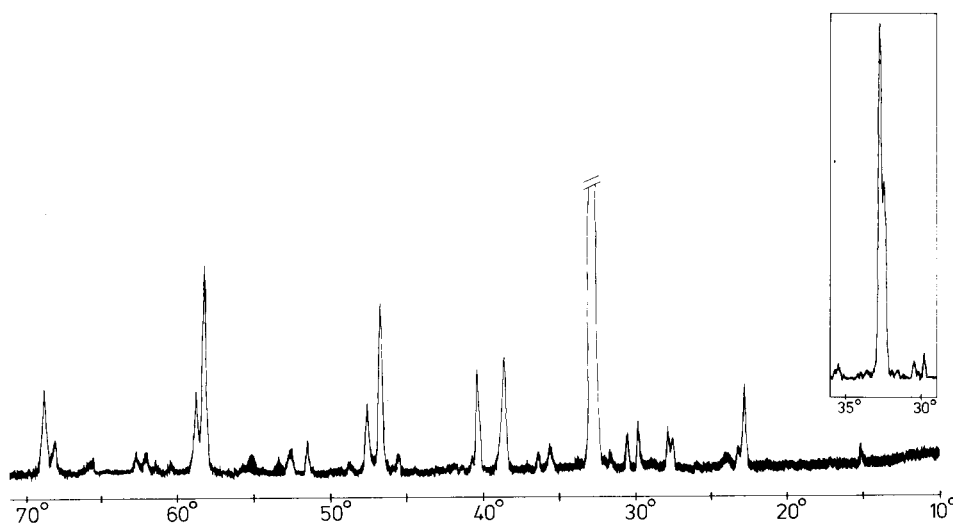


Fig. 1. Powder X-ray diffraction pattern for the single-phase $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ after calcination, including solid state reaction, of the powder obtained by citrate synthesis.

tions of the spectrum of fig. 1 together with the distance d between the scattering planes and the Cu K_α 2θ -values calculated with the orthorhombic lattice parameters $a = 3.82 \text{ \AA}$, $b = 3.89 \text{ \AA}$ and $c = 11.67 \text{ \AA}$. The observed intensities are taken relative to the intensity of the coinciding (110) and (103) reflections. The intensities measured by Cava et al. [4] are depicted for reasons of comparison.

We calculated the intensities of all reflections using the fractional coordinates obtained by Capponi et al. from powder neutron diffraction [5]. The square of the structure factor F was corrected for the number of contributing (hkl)-planes. Further we accounted for the LP-factor $(1 + \cos^2 2\theta) / \sin \theta \cdot \sin 2\theta$ and the correction for the varying divergence slit. The influence of preferential orientations was not considered. The results of the calculations are also included in the table. In general we found a very good agreement between observed and calculated intensities.

4. Resistance measurements

The resistances of the prepared samples were measured by a four terminal ac technique as a function of the temperature. The sample was placed in a copper housing together with a platinum resistance thermometer and cooled by a helium gas flow. The contact with the sample was realized by evaporated copper strips on to which the connecting wires could be easily attached.

A typical resistance versus temperature measurement of a sample prepared by citrate synthesis is given in fig. 2. The onset temperature is about 99 K whereas the sample is resistanceless at 91.2 K. The transition is sharp and does not exhibit a shoulder as is usually found in case of compounds consisting of more than one phase. This sharp transition could have been expected from the good X-ray spectrum. The samples prepared by the solid state reaction method show transition temperatures ($R = 0$) of about 89 K.

An interesting feature of the resistancelessness of the material is the possibility of levitation of a

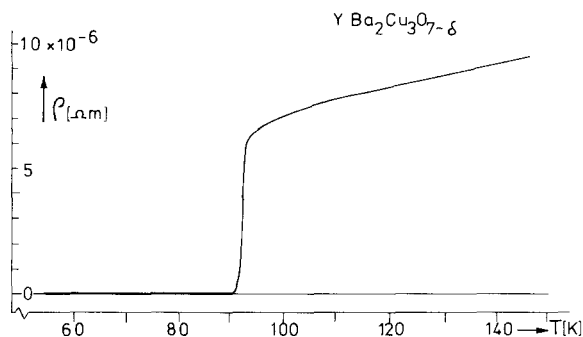


Fig. 2. The temperature dependence of the resistivity of the single-phase $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, obtained by citrate synthesis, ρ is decreasing a factor 2.4 between $T = 300 \text{ K}$ and $T = 100 \text{ K}$.

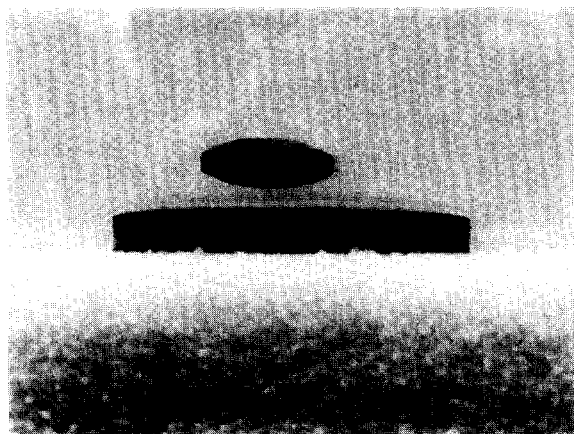


Fig. 3. Photograph of a small magnet, floating above $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ at liquid nitrogen temperature.

small magnet. In fig. 3 we show a photograph of a small magnet floating millimeters above one of our $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ samples at liquid nitrogen temperature.

5. Electron spin resonance

Electron spin resonance experiments on powdered samples were performed both at X- and Q-band frequencies. In fig. 4 we present a first-derivative absorption spectrum measured at a microwave frequency of 34.753 GHz. Some DPPH was added as a marker with a g -factor of 2.0036 and g -shifts, Δg , with respect to this marker are estimated to have an accuracy of

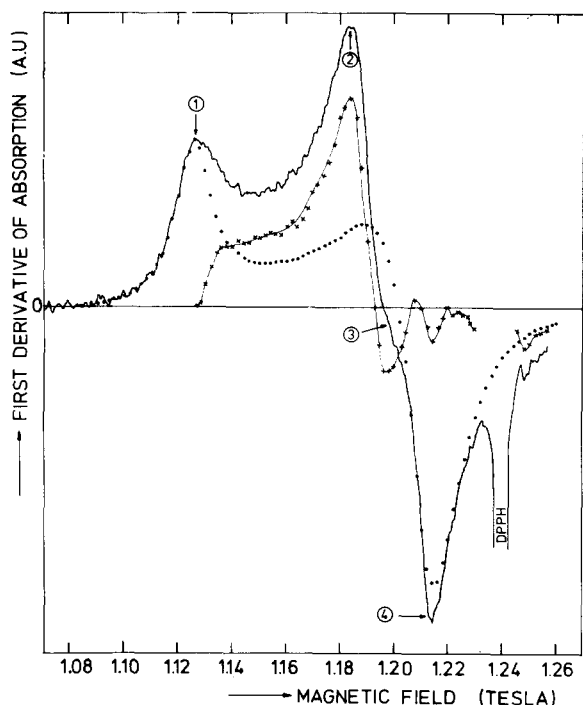


Fig. 4. Measured Q-band spectrum of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ including DPPH marker (noisy solid line). Simulated axial Cu^{2+} spectrum with $g_{\parallel} = 2.206$, $g_{\perp} = 2.053$, $\frac{1}{2}\Delta H_{pp\parallel} = 4.7$ mT and $\frac{1}{2}\Delta H_{pp\perp} = 8.5$ mT (dotted line). Difference spectrum that for the greater part may be attributed to Cu^{3+} with $g = 2.080$ and $\frac{1}{2}\Delta H_{pp} = 12$ mT (crossed line). All line shapes are assumed to be Lorentzian.

0.5% or $\Delta g = 0.001$, whichever is worst. The spectrum has three characteristic peaks 1, 2 and 4 and a shoulder 3. Apart from this shoulder and the fact that peaks 2 and 4 are widely separated this spectrum closely resembles that of a magnetic ion with axial symmetry with $g_{\parallel} > g_{\perp}$. From the top of peak 1 we obtain $g_{\parallel} = 2.206$, whereas from peak 4 a lower bound of 2.045 for g_{\perp} is derived.

Information about the symmetry of the Cu ions can be obtained from the crystal structure [5]. The Cu-I site is missing two oxygens of an octahedron (along the a -direction) and the Cu-II site one oxygen whereas the Cu ion moved from the center of the octahedron in the direction of the remaining oxygen along the c -direction. Both sites can be considered to have an octahedral oxygen environment with elongation along a fourfold axis.

It is known that for a cubic crystal field with a tetragonal distortion and effective spin $s = \frac{1}{2}$:

$$g_{\parallel} = 2 - 8 \frac{\lambda}{\Delta}, \quad g_{\perp} = 2 - 2 \frac{\lambda}{\Delta},$$

or

$$g_{\parallel} = 2 - 6 \frac{\lambda}{\Delta}, \quad g_{\perp} = 2,$$

with λ the spin-orbit coupling constant and Δ the cubic crystal field splitting [6]. It is clear from our measurements that the second possibility has to be excluded and this means that the $3d_{x^2-y^2}$ doublet of Cu^{2+} is the hole state of lowest energy. Using our estimate for g_{\parallel} we find $g_{\perp} = 2.053$. It is at once obvious that peak 4 corresponds to the latter g -value taking a finite line width into account, but peak 2 and shoulder 3 not.

We calculated powder spectra on a digital computer with a program [7] to simulate spectra for Cu^{2+} in an orthorhombic crystal field. The simulated spectrum is also plotted in fig. 4 together with a difference spectrum between measurements and simulations. It turned out that reasonable fits are obtained with the aforementioned g -values and taking as line widths $\frac{1}{2}\Delta H_{pp\parallel} \sim 4.8$ mT and $\frac{1}{2}\Delta H_{pp\perp} \sim 8.5$ mT. As we could not see any resolved hyperfine splitting we neglected its influence in the simulations. Furthermore it turned out that Lorentzian line widths gave better fits than the Gaussian line widths. Including any rhombicity, i.e. separating g_{\perp} into two slightly different g -values, did not improve our results. The difference spectrum has a g -value of 2.080 ± 0.005 which is very close to the g -value of Cu^{3+} in Al_2O_3 ($g_{\parallel} = 2.0788$, $g_{\perp} = 2.0772$ [6]). Part of the spectrum around $g = 2$ is due to CuO impurities in our sample, which was made by solid state reactions only with rather coarse grains. This particular sample was obtained from a sintered piece of material having a T_c of approximately 30 K as measured by its zero resistance. We also measured spectra from powders before and after sintering of which the latter have T_c 's of approximately 50 K and 90 K. All spectra, apart from the influence of CuO, which was no longer measurable, are equal apart from the fact that the signal-to-noise ratio gets worse

as T_c increases. This is due to the decreasing resistance at room temperature and the corresponding excessive loading of the microwave cavity.

Using the previously mentioned g -values, line widths and line shape we also simulated an esr spectrum at an X-band frequency of 9.51774 GHz, and compared this with a measured spectrum. Again there is an (almost) isotropic line with $g = 2.080$ and $\frac{1}{2}\Delta H_{pp} \sim 12$ mT which we ascribe to Cu^{3+} . By integrating this difference spectrum twice we obtained the intensity and compared this with the intensity of the simulated Cu^{2+} spectrum. The intensity is about 40% of that of the Cu^{2+} value. Using the fact that intensities are proportional to $S(S+1)$, assuming equidistant energy levels and neglecting anisotropies in the g -factor, we estimate that 14% of the Cu-ions are Cu^{3+} . The same value was arrived at using the calculated intensities of the simulated spectra of Cu^{2+} and those of Cu^{3+} with the same parameters as before and amplitudes that gave reasonable fits to the measured Q-band spectrum. With these values of the amplitudes about 70% of the total measured intensity in fig. 4 is accounted for. Hence we assume as a crude estimate for the oxygen deficiency δ in the formula $YBa_2Cu_3O_{7-\delta}$ the value 0.3 in order to maintain charge neutrality. If we apply the same procedure to a sample that was prepared with the citrate synthesis method we obtain $\delta \sim 0.4$ indicating a higher oxygen deficiency. This does not seem to influence the T_c -value very much for in both cases T_c -values of 90 K have been found.

We were not able to discriminate between the two possible sites for Cu^{2+} and Cu^{3+} . This could be due to small differences in cubic crystal field

strengths at both sites. Detailed crystal field calculations are started to clarify this matter.

Acknowledgements

The authors would like to thank H. Kruidhof for his indispensable help preparing the samples, K. Keizer and S. Harkema for the helpful discussions, the latter also for calculating the structure factors.

Note added in proof

It cannot be excluded that the ESR spectrum is (partly) due to the so-called green phase Y_2BaCuO_5 .

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