EXAFS analysis of intermediate phases in the synthesis of the Y Ba₂ Cu 3O_{7-x} high-T_c superconductor from xerogel

I. Arcon, M. Bele, M. Hribar, A. Kodre, S. Pejovnik, M. Stuhec, W. Drube

► To cite this version:

I. Arcon, M. Bele, M. Hribar, A. Kodre, S. Pejovnik, et al.. EXAFS analysis of intermediate phases in the synthesis of the Y Ba₂ Cu 3O_{7-x} high-T_c superconductor from xerogel. Journal de Physique IV Proceedings, 1994, 04 (C9), pp.C9-105-C9-108. 10.1051/jp4:1994913 . jpa-00253473

HAL Id: jpa-00253473

<https://hal.science/jpa-00253473>

Submitted on 1 Jan 1994

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

EXAFS analysis of intermediate phases in the synthesis of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ high- T_c superconductor from xerogel

I. Arčon, M. Bele*, M. Hribar, A. Kodre, S. Pejovnik*, M. Štuhec and W. Drube**

Jožef Stefan Institute, Jamova 39, 61111 Ljubljana, and Department of Physics, University of Ljubljana, Slovenia

** National Institute of Chemistry, Hajdrihova 19, 61115 Ljubljana, Slovenia*

*** HASYLAB at DESY, Hamburg, Germany*

Abstract: In the synthesis of superconducting cuprate ceramics starting from gels, the advantage of stoichiometric homogeneity of the constituent atoms on the molecular level is exploited. However, x-ray diffraction analysis of samples taken in consecutive temperature points in the process of calcination shows formation of a number of well-crystallized intermediary products. EXAFS spectrometry gives additional insight into the process, providing the information on the neighborhood of constituent atoms in the crystalline as well as amorphous phase.

1. INTRODUCTION

For the study of the high- T_c superconducting ceramics, as well as for their practical application, high quality of the product is essential. Considerable improvement has been achieved with the adoption of sol-gel preparation methods which ensure the mixing of the starting materials at the molecular level, resulting in a uniform solid-state reaction with minimal formation of undesired phases [1]. The reaction is completed in a shorter time at the lowest possible temperature.

However, in the process of synthesis of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ from xerogel, intermediate compounds have been observed to form crystalline phases, whereby the advantage of the initial homogeneity can be partially lost [2]. In this paper, an EXAFS study of the intermediates in conjunction with the x-ray diffraction analysis is reported. The information on nearest-neighbour distances and coordination numbers of Cu and Ba atoms in ordered and disordered phases, extracted from the EXAFS analysis, complements the diffraction data on lattice constants and crystallite sizes.

2. EXPERIMENTS

In a new method the superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ceramic is prepared via a sol-gel route using Y_2O_3 , $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$, $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ and CH_3COOH [3]. By vacuum drying, a xerogel with

the nominal composition $Y : Ba : Cu : CH_3COO = 1 : 2 : 3 : 7.7$ is obtained and calcinated at 410°C . Powders were pressed in pellets and sintered at 900° in oxygen.

Samples of xerogel were taken during the heating process at consecutive temperature points corresponding to stable thermogravimetric phases. X-ray diffraction was measured on powdered samples, using Cu K alpha line, in steps of 0.02° from 5° to 70° .

EXAFS spectra above Cu K and Ba L_3 edges of the samples were measured at the EXAFS II beamline in HASYLAB at DESY. The beam is focused with the gold-coated toroidal mirror onto a double crystal Si(111) monochromator with energy resolution of $\Delta E/E = 2 \cdot 10^{-4}$. Energy regions of 800 eV above the Cu K edge and 400 eV above the Ba L_3 edge were scanned in steps of 1 eV.

3. RESULTS

Diffraction spectra (Fig. 1) show that the xerogel is amorphous up to the temperature of 230°C where formation of very small CuO crystals is observed (Table 1). At 250°C , relatively large Cu_2O crystals appear, their proportion growing till 285°C , where CuO crystals completely vanish. At higher temperatures the trend is reversed until at 650°C only CuO, accompanied with BaCO_3 and Y_2O_3 is identified. Out of these, the superconducting phase $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ is formed at 900°C .

The standard Fourier-transforms (FT) of EXAFS spectra are shown in Fig 2. Amorphous phases are characterized by a single peak in FT, showing that only the shell of first neighbours around the investigated atom is well-defined. Further peaks indicate the existence of long-range order, corresponding to crystalline phases. Positions of the peaks are used to extract average first- and second-neighbour distances. From the size of the first peak, the coordination number of neighbour oxygen atoms can be deduced. The results, together with diffraction data, are shown in Table I.

The average neighbour distances from the EXAFS analysis agree with values from the crystal lattice data for phases, identified in the diffraction measurements. Below 230°C , Cu atoms are imbedded in amorphous phase with $R=1.95 \text{ \AA}$ and coordination number 4. At 230°C , growth of CuO crystals is indicated by the second peak in FT at $R=2.4 \text{ \AA}$. At 285°C and 410°C the coordination number of the oxygen atoms in the first shell changes from 4, characteristic of the CuO crystal structure, to 2, corresponding to Cu_2O crystalline structure. In the superconducting phase the number of Cu nearest neighbours is again 4. Average valence of Cu atom in the samples, deduced from the position of the K edge in the absorption spectra, agrees with diffraction and EXAFS data.

Barium compounds in the xerogel are amorphous up to $T= 410^\circ\text{C}$. Coordination number of the Ba first shell neighbours is constant in the amorphous phase. The atom is incorporated into the crystalline phase at 650°C .

4. CONCLUSION

EXAFS analysis supports and extends the diffraction data, testifying conclusively of the different histories of Cu and Ba atoms in the synthesis of the final product. The EXAFS of yttrium, although not attainable with the same resolution, should complete the picture. The distinct advantage of

Figure 1 X-ray diffraction spectra of the xerogel samples at selected temperature points in the process of synthesis of the superconductor ceramics.

Figure 2 Magnitude of the Fourier transform of the Cu K-edge (a) and Ba L_3 -edge (b) EXAFS spectra of the xerogel at the selected temperature points.

EXAFS to provide data on the amorphous phase can be used in further research to establish to what extent the synthesis of the superconducting ceramics may be inhibited or mediated by the formation of the crystallites of Cu oxides.

Table I. Diffraction and EXAFS data for consecutive temperature points: crystal phases, identified in X-ray diffraction; average crystal size, estimated from the width of the diffraction maxima; average distances (R_1 , R_2) and the coordination number (N) of the first and second neighbours. (*)-unidentified crystal phases.

	DIFFRACTION		EXAFS			
			Copper			Barium
T [°C]	identified crystallites	average crystal size [Å]	R_1 [Å]	N	R_2 [Å]	R_1 [Å]
60	amorphous		1.95	4		2.66
108	amorphous		1.95	4		2.66
145	amorphous		1.95	4		2.66
210	amorphous		1.93	4		2.66
230	CuO	65	1.95	4	2.70	2.66
250	Cu ₂ O, CuO	>2000, 55	1.93	3	2.54	2.66
285	Cu ₂ O	>2000	1.77	2	2.82	2.66
410	Cu ₂ O, CuO, (*)	440, 160	1.85	2	2.72	2.61
650	CuO, BaCO ₃ , Y ₂ O ₃ (*)	180, >2000, >2000				
900	YBa ₂ Cu ₃ O _{7-x} (123)	>2000	1.95	4	3.28	3.26

Acknowledgements: This work was supported by Ministry of Science and Technology of Slovenia, and Internationales Büro des Forschungszentrum, Jülich.

5. REFERENCES

- [1] Barboux P., Tarascon J. M., Greene L. H., Hull G. W., and Bagley B. G., J. Appl. Phys., **63** (1988) 2725-2729
- [2] Chu C., and Dunn B., J. Am. Ceram. Soc., **70** (1987) C-375 - C-377
- [3] Pejovnik S., Bele M., Patent appl. SLO-9300578 (1993)
Patent Office, Čopova 14, 61000 Ljubljana. Slovenia.