

A comparative study of $\text{YBa}_2\text{Cu}_4\text{O}_8$ (Y-124) superconductors prepared by a sol–gel method

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Abstract

The aqueous sol–gel synthesis technique for the preparation of $\text{YBa}_2\text{Cu}_4\text{O}_8$ (Y-124) superconductor was studied using two different complexing agents with the same chemical composition, namely L-(+)-tartaric (natural) and DL-tartaric (synthetic) acids. The characterization of Y–Ba–Cu–O gels by XRD and TGA/DTA measurements showed the individuality of precursor gels and a high level of homogeneity. On the other hand, the morphological features of the gels observed by SEM measurements were slightly different. The ceramic samples calcined for 30 h at 780 °C in a flowing oxygen atmosphere contained homogeneous Y-124 crystallites as a major phase, as was shown by XRD analysis. The T_C (onset) observed by resistivity and magnetic susceptibility measurements was approximately the same for the both samples (78–80 K). However, the temperature–resistivity and temperature–magnetic susceptibility dependences were found to be different for the Y-124 samples synthesized by different sol–gel procedures. Such behaviour was discussed in correlation with the morphological properties of the prepared samples.

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1. Introduction

The $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ [1,2], often called “Y-123” or “123”, belongs to a family which can be described with the general formula $\text{Y}_2\text{Ba}_4\text{Cu}_{6+n}\text{O}_{14+n}$ ($n = 0, 1, 2$) [3–5]. High T_C superconducting $\text{YBa}_2\text{Cu}_4\text{O}_8$ (Y-124 or 124) is the $n = 2$ member of the above homologous series of compounds. The first synthesis of $\text{YBa}_2\text{Cu}_4\text{O}_8$ in bulk phase and subsequent preparations were carried out under high oxygen pressure [6,7]. The 124 superconductor exhibits a transition temperature, T_C at around 80 K, and unlike the 123 phase its oxygen content has excellent thermal stability. The characteristic properties make the 124 phase very interesting from a theoretical point of view as a slightly different model

system for testing the general trends of high- T_C materials and also in view of possible applications [8–12].

Over the last few decades, sol–gel techniques have been used to prepare variety mixed-metal oxides. In these sol–gel processes, good quality of the oxide products was expected primarily due to the purity of the precursor materials used and chemical homogeneity obtained from the synthesis route [13–18]. The molecular level mixing and the tendency of partially hydrolysed species to form extended networks facilitate the structure evolution thereby lowering the crystallisation temperature of multicomponent metal oxide ceramics. Recently we described the use of an aqueous sol–gel method for the synthesis of monophasic non-substituted $\text{YBa}_2\text{Cu}_4\text{O}_8$, as well as superconducting Y-124 samples substituted in the yttrium, barium and copper positions by other elements [19–22]. Also, it was shown the importance of nature of the complexing agent in the sol–gel process in order to obtain monophasic supercon-

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ducting Y-124 oxide [23]. The aim of this study was to investigate the influence of two complexing agents having the same chemical composition, namely L-(+)-tartaric (natural) and DL-tartaric (synthetic) acids, on the morphological characteristics and superconducting properties of YBa₂Cu₄O₈ superconductor prepared by an aqueous acetate–tartrate sol–gel route. In addition, the purpose of this study was to show that adjusting the nature of complexing agent during sol–gel preparation of superconducting cuprate can be used to control the physical properties of the end product.

2. Experimental

The YBa₂Cu₄O₈ superconducting samples were prepared by two acetate–tartrate sol–gel routes. As starting compounds stoichiometric amounts of Y₂O₃, Cu(CH₃COO)₂ · H₂O, and Ba(CH₃COO)₂, all of them analytical grade, were used. In the sol–gel process Y₂O₃ first was dissolved in 0.2 M acetic acid at 55–60 °C. Next, Ba(CH₃COO)₂ and Cu(CH₃COO)₂ · H₂O, both of them dissolved in a small amount of distilled water, were added with intermediate stirring during several hours at the same temperature. Finally, solution of tartaric acid ((a) L-(+)-tartaric acid; synthesis route NSG and (b) DL-tartaric acid; synthesis route SSG) in water was added to prevent crystallization of metal acetates or hydroxides during gelation. The obtained solutions were concentrated during about 8 h at 60–65 °C in an open beaker. Under continuous stirring the transparent blue gels have formed. After further drying in an oven at 80 °C fine grained blue powders were obtained. The precursor powders were calcined for 10 h at 780 °C in flowing oxygen, reground in an agate mortar, pelletized and again heated for 20 h at 780 °C in a flowing oxygen atmosphere at ambient pressure with intermediate regrinding and repelletizing.

The synthesized Y-124 oxides were characterized by means of powder X-ray diffraction analysis performed with a Philips MPD 1880 diffractometer, using Cu Kα₁ radiation. Scanning electron microscopes (SEM) CAM SCAN S4 and JEOL 820 were used to study the morphology and microstructure of the gel precursor and ceramic samples. The cation content in the obtained ceramics was analyzed by energy-dispersive spectrometry (EDS) in a JEOL 820 scanning electron microscope, using L, K lines. The TGA/DTA measurements were performed on a STA 490 analyzer (Netzsch) in oxygen at a heating rate of 5 °C/min (sample weight 25–30 mg). A standard four-probe technique was used for measuring the temperature dependence of the resistivity in the range 20–300 K. The diamagnetic susceptibility was determined with a Lake Shore 7000 AC susceptometer.

The distribution of Cu(II), Y(III) and Ba(II) among the acetate–tartrate complexes and the concentration of free (uncomplexed) metal ions were calculated by solving the system of non-linear equations in terms of the Newton iteration method [24]. The values of equilibrium constants

Table 1
Equilibrium constants for system Ba(II), Cu(II), Y(III) – acetate, tartrate

Reaction	Equilibrium constant
Ba ²⁺ + CH ₃ COO ⁻ ⇌ Ba(CH ₃ COO) ⁺	log β ₁ = 1.15
Ba ²⁺ + Tart ²⁻ ⇌ BaTart	log β ₁ = 1.68
Cu ²⁺ + CH ₃ COO ⁻ ⇌ Cu(CH ₃ COO) ⁺	log β ₁ = 2.23
Cu ²⁺ + 2CH ₃ COO ⁻ ⇌ Cu(CH ₃ COO) ₂	log β ₂ = 3.63
Cu ²⁺ + Tart ²⁻ ⇌ CuTart	log β ₁ = 3.25
Cu ²⁺ + 2Tart ²⁻ ⇌ CuTart ₂ ⁻	log β ₂ = 4.90
Y ³⁺ + CH ₃ COO ⁻ ⇌ Y(CH ₃ COO) ²⁺	log β ₁ = 1.53
Y ³⁺ + 2CH ₃ COO ⁻ ⇌ Y(CH ₃ COO) ₂ ⁺	log β ₂ = 2.66
Y ³⁺ + 3CH ₃ COO ⁻ ⇌ Y(CH ₃ COO) ₃	log β ₃ = 3.4
Y ³⁺ + Tart ²⁻ ⇌ YTart ⁺	log β ₁ = 4.07
Y ³⁺ + 2Tart ²⁻ ⇌ YTart ₂ ⁻	log β ₂ = 6.89
Y ³⁺ + OH ⁻ ⇌ Y(OH) ²⁺	log β ₁ = 10.5
Y ³⁺ + 2OH ⁻ ⇌ Y(OH) ₂ ⁺	log β ₂ = 19.8
Y ³⁺ + Tart ²⁻ + OH ⁻ ⇌ YTart(OH)	log β = 11.7
Y ³⁺ + 2Cu ²⁺ + 3Tart ²⁻ + 5OH ⁻ ⇌ Cu ₂ YTart ₃ (OH) ₅ ⁴⁻	log β = 54.4
CH ₃ COOH ⇌ CH ₃ COO ⁻ + H ⁺	log K _a = -4.56
H ₂ Tart ⇌ HTart ⁻ + H ⁺	log K _{a1} = -2.89
HTart ⁻ ⇌ Tart ²⁻ + H ⁺	log K _a = -4.52
Cu ²⁺ + 2OH ⁻ ⇌ Cu(OH) ₂	log K _{s0} = -18.2
Y ³⁺ + 3OH ⁻ ⇌ Y(OH) ₃	log K _{s0} = -24.5

used were taken from [25–29] and are listed in Table 1. The following conditions were used for the speciation analysis in the pH range from 2 to 7: (i) Y(III) – 0.03125 M; Ba – 0.0625 M, Cu(II) – 0.125 M, acetate – 0.575 M, tartrate – 0.0625 M; (ii) Y(III) – 0.3125 M; Ba – 0.625 M, Cu(II) – 1.25 M, acetate – 5.75 M, tartrate – 0.625 M.

3. Results and discussion

3.1. Distribution of physico-chemical forms

The calculations showed that the distribution of Y(III), Ba(II) and Cu(II) among the complexes in the acetate–tartrate solutions depends on pH of solution (Figs. 1–3). The distribution of physico-chemical forms of Y(III) in acetate–tartrate solutions is shown in Fig. 1. In the range of pH from 2 up to 5.5 yttrium tartrates are predominating species in the system. Yttrium acetates and Y(III) hydroxy-complexes predominate at higher pH. Ba(II) ions exist in three forms in the solutions. Depending on the total concentration, Ba(II) aqua-ions prevail till pH 3–4, and again Ba(II)–monoacetate complex predominates with further increase in pH (see Fig. 2). However, a part of barium exists in the form of barium tartrate in the whole investigated range of pH. It is evident that Cu(II) acetate and tartrate complexes prevail at pH over 2.5 independent on the total concentration of copper.

The calculations of free metal ions concentration and its comparison with data about insoluble hydroxides formation are presented in Fig. 4. As seen, the formation of Cu(OH)₂ precipitate during gelation process in the acetate–tartrate system possibly could start at pH over ~7.5, while Y(OH)₃ precipitation was not expected in the investigated pH range.

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