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PREPARATION AND CHARACTERIZATION OF SUPERCONDUCTING $YBa_2(Cu_{1-x}Cr_x)_4O_8$ OXIDES BY THERMAL ANALYSIS

G. Nenartaviciene[1], *K. Tõnsuaadu*[2], *D. Jasaitis*[1], *A. Beganskiene*[1] *and A. Kareiva*[1*]

[1]Department of General and Inorganic Chemistry, Vilnius University, Naugarduko 24, 03225 Vilnius, Lithuania
[2]Laboratory of Inorganic Materials, Tallinn University of Technology, Ehitajate tee 5, 19086 Tallinn, Estonia

In this study the formation of chromium substituted $YBa_2Cu_4O_8$ (Y-124) superconductors has been investigated by TG/DTA measurements. The $YBa_2(Cu_{1-x}Cr_x)_4O_8$ ceramics with nominal compositions of x=0.01, 0.03, 0.05, 0.10 and 0.20 have been prepared by an aqueous sol–gel method using aqueous mixtures of the corresponding metal acetates and nitrates. Homogeneous precursor gels were obtained by complexing metal ions with tartaric acid. To assist the interpretation of the results obtained the synthesis products were additionally characterized by X-ray powder diffraction (XRD) and resistivity measurements. It was determined that doping the $YBa_2Cu_4O_8$ phase with chromium has a strong effect on the phase purity and superconducting properties of the synthesis products.

Keywords: *chromium substitution, sol–gel synthesis, TG/DTA, Y-124 superconductor*

Introduction

The studies on various substitutions in oxide superconducting systems have proven to be of great importance since considerable changes in critical transition temperature of superconductivity (T_c) are usually observed [1–4]. The interest in adding a small amount of some additional metal ion in the parent compound lies in the fact that doping basically can vary the hole concentration in a controlled manner thus influencing the superconducting properties of the materials obtained [5].

It is well recognized that the $YBa_2Cu_4O_8$ (Y-124) superconducting phase is thermodynamically stable, stoichiometric and thus is an ideal system to study different substitutional effects [6–11]. It is also well known that thermal characterization of synthesized samples is important both for control of the reaction process and for the properties of materials obtained [12–16]. In some cases, chimie douce synthesis methods, especially those based on carbon-containing precursors could produce superconducting materials with a broadened transition temperature. It is believed, that the origin of such degradation of superconducting properties is the retention of carbon in the structure of the superconductor [17]. The decomposition reactions of various metal carbonates during calcination of different multimetallic precursors could be successfully investigated by thermogravimetric (TG) measurements [18–20]. TG coupled with FTIR provides very important information of the decomposition products and the evolved gases [21]. As an example of such study, the detailed investigation of the decomposition of the oxalate precursors and the stability of the $YBa_2Cu_4O_8$ superconductor was reported by Mullens *et al.* [22]. Thermogravimetric experiments are very useful to solve the nonstoichiometry problems, which are the central ones in the solid-state chemistry [17]. Several oxygen deficient ternary cuprates having different superconducting properties have been determined during TG studies of the nonstoichiometric regions in different superconducting systems [23–25].

In this context, thermal analysis is a versatile group of techniques which can be used to monitor the preparative studies [26–28]. Therefore, to understand more completely the mechanisms of the formation of substituted Y-124 cuprates we report here the results of application of TG/DTA methods for the systematic investigation of sol–gel process in the Y–Ba–Cu(Cr)–O system, characterization of intermediates and the end products obtained during the heat treatments.

Experimental

The $YBa_2(Cu_{1-x}Cr_x)_4O_8$ samples with x=0.01, 0.03, 0.05, 0.10 and 0.20 were prepared by an acetate–tartrate sol–gel method. As starting compounds, stoichiometric amounts of Y_2O_3, $Ba(CH_3COO)_2$, $Cu(CH_3COO)_2·H_2O$ and $Cr(NO_3)_3·9H_2O$, all of them analytical grade (Aldrich), were used. In the sol–gel process Y_2O_3 first was dissolved in 0.2 M acetic acid at 55–60°C. Next, $Ba(CH_3COO)_2$ and $Cu(CH_3COO)_2·H_2O$ or appropriate

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[*] Author for correspondence: aivaras.kareiva@chf.vu.lt

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Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

mixtures of $Cr(NO_3)_3{\cdot}9H_2O$ and $Cu(CH_3COO)_2{\cdot}H_2O$, all of them dissolved in a small amount of distilled water, were added with intermediate stirring during several hours at the same temperature. The obtained solutions were concentrated during about 8 h at 60–65°C in an open beaker. Under continuous stirring the transparent blue Y–Ba–Cu(Cr)–O gels were formed. After further drying in an oven at 80°C fine grained blue powders were obtained. The precursor gel powders were calcined for 10 h at 700°C in flowing oxygen, reground in an agate mortar, and again heated for 20 h at 800°C, again reground, pelletized and annealed for 20 h at 800°C in a flowing oxygen atmosphere at ambient pressure.

In this study the chromium substitution effects in the $YBa_2Cu_4O_8$ superconductor has been investigated by TG/DTA measurements in flowing air atmosphere using Setaram TG-DSC12 and STA 490 analyzers. The mass of specimens was 20.45–25.28 mg. The synthesized samples were characterized by X-ray powder analysis performed in a Siemens D-500 diffractometer, using $CuK_{\alpha 1}$ radiation. Superconducting properties were determined by resistivity measurements using a standard four-point technique.

Results and discussion

Characterization of the gel precursors

Thermal behaviour of the Y–Ba–Cu(Cr)–O precursor gels was studied in flowing air up to 1000°C using a heating rate of 10°C min^{-1}. Interestingly, thermal behaviour of the TG curves was qualitatively the same regardless of the chromium substitution level. TG curves for the three representative Y–Ba–Cu(Cr)–O precursor gels are shown in Fig. 1. Obviously, the TG curves confirm that in all cases the thermal decomposition proceeded in a similar way. The TG curves reveal three main mass losses to occur in the temperature ranges ~20–185, ~185–260 and ~260–400°C. The mass loss below 185°C (~5.5–8.8%) is due to a loss of crystallization water and/or water from the coordination sphere of the metal complexes and the evaporation of water and solvent molecules. Besides, the decomposition of $Cr(NO_3)_3{\cdot}9H_2O$ to Cr_2O_3 also occurs in the same temperature range (Fig. 2). The further two significant decomposition steps observed (~185–260 and ~260–400°C) can be attributed to the pyrolysis of intermediate species formed during the gelation process. In the temperature range 185–260°C, mainly the decomposition of copper constituent is observed [29]. The decomposition of the barium acetate–tartrate gel occurs in three steps with main mass loss observed between 280 and 345°C [29]. As seen from the TG results, the final mass loss (~3.7–6.5%) on the TG curves of the gel was observed in the temperature range 800–1000°C.

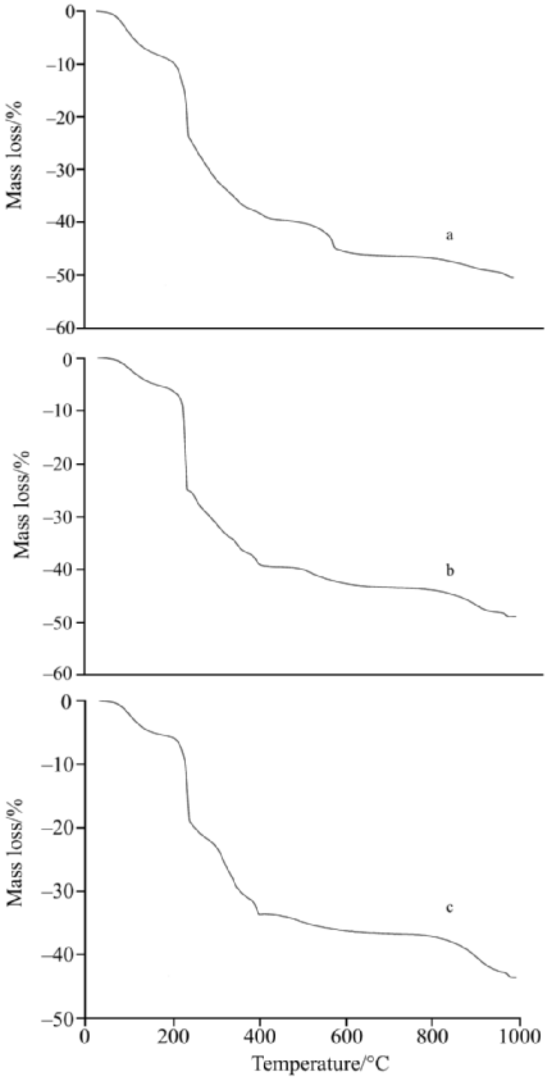

Fig. 1 TG curves recorded in flowing air for Y–Ba–Cu(Cr)–O precursor gels with different substitutional level of Cr: a – 3, b – 10 and c – 20%. Heating rate 10°C min^{-1}

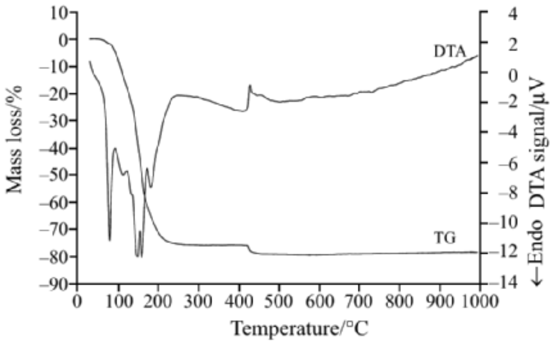

Fig. 2 TG/DTA curves of $Cr(NO_3)_3{\cdot}9H_2O$ recorded in flowing air. Heating rate 10°C min^{-1}

The thermal decomposition behaviour is associated with endothermic and exothermic effects in the DTA curves. The three representative DTA curves for the Y–Ba–Cu(Cr)–O precursor gels are shown in

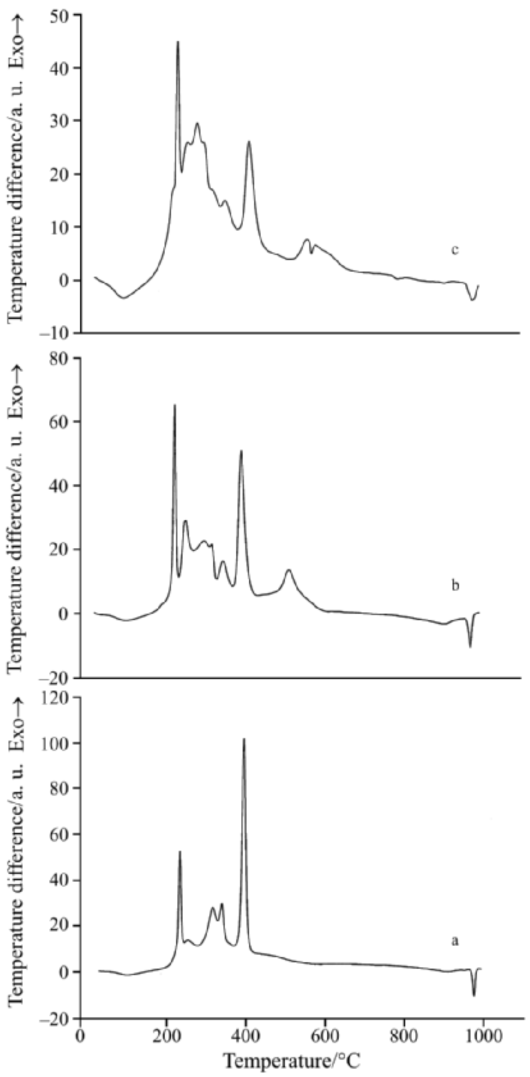

Fig. 3 DTA curves recorded in flowing air for Y–Ba–Cu(Cr)–O precursor gels with different substitutional level of Cr: a – 3, b – 10 and c – 20%. Heating rate 10°C min^{-1}

Fig. 3. The first decomposition step, assignable to removal of adsorbed and chemisorbed water, is indicated by a broad endothermic peak around 100°C on the DTA curves. Exothermic peaks from 235–240°C to 400°C in the DTA curves are due to the pyrolysis processes occurring during further heating of the gel samples. Interesting feature observed is that the intensity of the exothermic peak at 400°C predominates at low substitutional level of Cr (up to 5%). However, starting from Y–Ba–Cu(Cr)–O precursor gel with 10% of Cr the prevailing exothermic peak is observed at lower temperatures (around 235–240°C).

The final mass loss on the TG curves observed in the temperature range 800–1000°C is accompanied by two very weak endothermic peaks around 800–900°C and one more intensive endothermic peak at 975°C. The nature of these peaks is sufficiently clear. In the temperature range of 800–900°C the $BaCO_3$ remaining undergoes an endothermic decarbonation reaction to BaO (which simultaneously reacts with other oxides) while carbon oxide is released [30]. These peaks could also correspond to the decomposition of the intermediate oxycarbonate $Y_2O_2CO_3$ to the oxide which occurs in the temperature range 600–800°C depending on the atmosphere used [29]. Besides the nature of the exothermic peaks at 975°C in the DTA curves can be associated with the decomposition of Y-124 particles to Y-123 and CuO phases [29]. It is well known when the Y-123 phase is heated in an oxidizing atmosphere it shows a reversible mass loss due to release of oxygen from the single Cu–O chains [17]. Thus the final endothermic peak above 975°C can be also attributed to the release of oxygen from the Y-123 phase.

Thus, thermal characterization of the gel samples yields information about mechanisms of thermal decomposition of the precursor, i.e. temperatures (or temperature intervals) of most important changes in mass. The optimum conditions for solid-state reaction could be also determined. According to the TG data the final annealing temperature for the preparation of Y-124 oxide should be around 800°C which is in agreement with previous studies [29, 31].

Characterization of the intermediates

In general, most of the syntheses by the sol–gel technique are based on carbon-containing precursors. Thus, the formation of metal carbonate ($BaCO_3$ or $CaCO_3$) is a major problem when sintering the superconducting materials. Characterization of the intermediates is interesting from the theoretical point to understand the possible mechanisms of the formation of the desired superconducting phase. Therefore the Y–Ba–Cu(Cr)–O precursor gels were calcined for 10 h at 700°C in flowing oxygen atmosphere. It was determined that all the specimens synthesized at 700°C were non-superconducting, and these non-superconduting samples exhibited only semiconducting behaviour. The results of resistivity *vs*. temperature measurements for the representative Cr(5%)-substituted Y-124 sample are shown in Fig. 4. Apparently, these ceramic powders may contain various impurity phases which could be responsible for the observed temperature dependence of their conductivity.

In order to detect the carbonate impurities in the synthesized (at 700°C) samples thermogravimetric measurements were performed. Figure 5 shows the TG curves obtained at heating rate of 2°C min^{-1} for the Y–Ba–Cu(Cr)–O precursor gels preheated at 700°C. As seen, in all cases the decomposition of carbonate or oxycarbonate phases at around 800°C takes place. Thus, it is obvious from the TG measurements that sig-

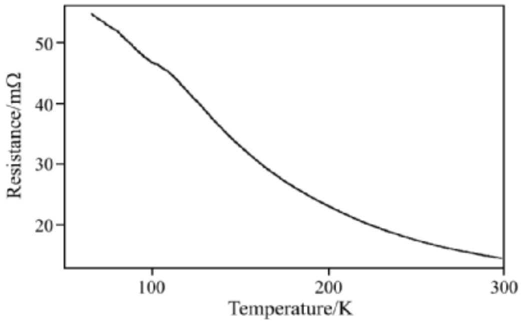

Fig. 4 Resistivity *vs.* temperature for the calcined at 700°C Y–Ba–Cu(Cr)–O precursor gel with 5% of Cr

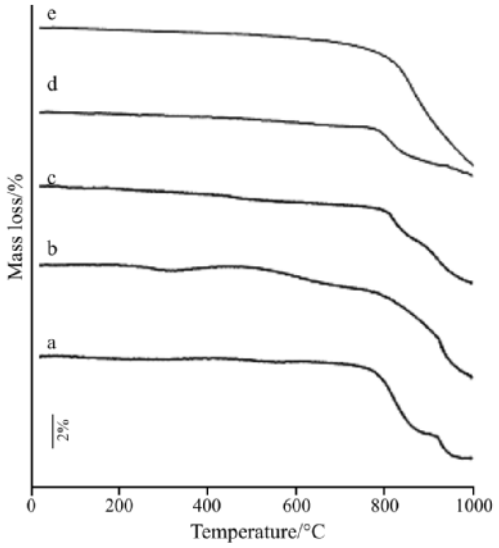

Fig. 5 TG curves recorded in flowing air for the calcined at 700°C Y–Ba–Cu(Cr)–O precursor gels with different substitutional level of Cr: a – 1, b – 3, c – 5, d – 10 and e – 20%. Heating rate 2°C min^{-1}

nificant amount of carbonate-containing phases ($BaCO_3$, $Y_2O_2CO_3$, $YBa_2Cu_{2.95}(CO_3)_{0.35}O_{6.6}$ or others) [20, 29] have formed during the initial calcination of Y–Ba–Cu(Cr)–O precursor gel samples.

This reaction mechanism is supported by X-ray diffraction analysis data. Annealing at 700°C produced a wide variety of mixed-metal oxides and carbonates having different chemical composition. The most intensive peaks present in all XRD patterns around 2θ=24–25° indicated the presence of a large amount of unreacted $BaCO_3$ (PDF 5-378) in the intermediate products. For instance, the X-ray diffraction peaks around 2θ=27–29° represent the most intensive diffraction lines of $BaCuO_2$ and $Ba_2Cu_3O_{5+x}$ (PDF 38-1402 and PDF 40-312, respectively). According to JCPDS© 1991 and 1996 reference data, in the region of 2θ=29–40° most of the peaks could be attributed to the $Ba_4Y_2O_7$ (PDF 28-0163) and CuO (PDF 5-661) phases.

Characterization of the end products

The observed T_c (onset), T_c (zero) and ΔT_c values for $YBa_2(Cu_{1-x}Cr_x)_4O_8$ samples are plotted as a function of x, as shown in Fig. 6. As seen in Fig. 6, the onset critical temperature of superconductivity monotonically decreases with increasing substitutional level of chromium. Resistivity measurements performed on the $YBa_2(Cu_{0.99}Cr_{0.01})_4O_8$ sample show a sharp superconducting transition with T_c (onset)=70 K. The T_c (onset) decreased to 68 K for $YBa_2(Cu_{0.97}Cr_{0.03})_4O_8$, to 65 K for $YBa_2(Cu_{0.95}Cr_{0.05})_4O_8$, and down to about 60 K for the $YBa_2(Cu_{0.9}Cr_{0.1})_4O_8$ sample. The resistivity in the normal conducting state increases with the number of Cr dopant sites which probably act as dissipation centres for electron transport. It is interesting to note, that the $YBa_2(Cu_{1-x}Cr_x)_4O_8$ samples with $x \geq 0.10$ exhibited only semiconducting behaviour indicating the loss of superconductivity at >10% Cr doping.

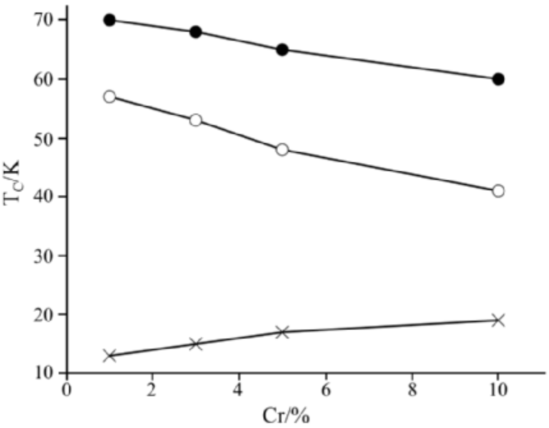

Fig. 6 Evolution of ● – T_c (onset), ○ – T_c (zero) and × – ΔT_c with chromium content in superconducting $YBa_2(Cu_{1-x}Cr_x)_4O_8$ as determined by resistivity measurements

In order to detect small amounts of Y-123 and Y-247 impurities the differences in the oxygen stability might be utilized [17, 30]. Therefore, the phase purity of the $YBa_2(Cu_{1-x}Cr_x)_4O_8$ samples synthesized in this work was checked by TG measurements. Figure 7 shows the TG curves of $YBa_2(Cu_{1-x}Cr_x)_4O_8$ samples obtained upon heating the compounds in air. Apparently, no indication of mass loss could be seen below ~800°C for the superconducting $YBa_2(Cu_{0.99}Cr_{0.01})_4O_8$, $YBa_2(Cu_{0.97}Cr_{0.03})_4O_8$ and $YBa_2(Cu_{0.95}Cr_{0.05})_4O_8$ samples. The results clearly indicate that these three samples mainly contain pure Y-124. However, for the next two samples ($YBa_2(Cu_{0.9}Cr_{0.1})_4O_8$ and $YBa_2(Cu_{0.8}Cr_{0.2})_4O_8$) the additional mass loss around 400–500°C is evident. Therefore we can conclude that using TG analysis we have established the formation of $YBa_2Cu_3O_{7-\delta}$ and/or $Y_2Ba_4Cu_7O_{15}$ phases in the Cr-substituted Y-124 samples when

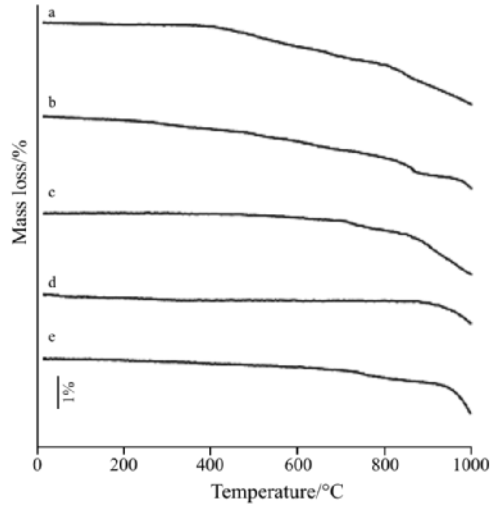

Fig. 7 TG curves recorded in flowing air for the $YBa_2(Cu_{1-x}Cr_x)_4O_8$ samples with different substitutional level of Cr: a – 1, b – 3, c – 5, d – 10 and e – 20%. Heating rate 2°C min^{-1}

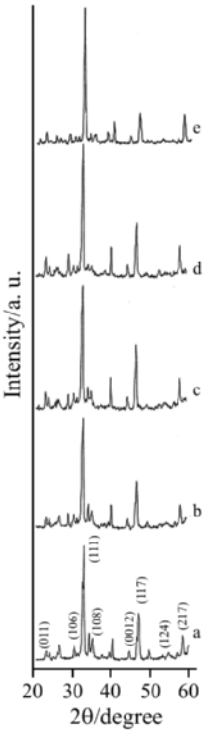

Fig. 8 Powder X-ray diffraction patterns of $YBa_2(Cu_{1-x}Cr_x)_4O_8$ samples: a – x=0.01, b – x=0.03, c – x=0.05, d – x=0.10, e – x=0.20

higher substitutional level of chromium was used [29, 31]. These results were found to be in a good agreement with the XRD results.

In Fig. 8 the XRD patterns of the $YBa_2(Cu_{1-x}Cr_x)_4O_8$ samples are presented. According to XRD analysis fully crystallized single-phase oxide $YBa_2(Cu_{0.99}Cr_{0.01})_4O_8$ with the well developed Y-124 crystal structure has been formed. As seen, all single lines can be indexed, and no unindexed lines could be observed. The Y-124 pattern is dominant also in the 3 and 5% Cr samples. According to X-ray diffraction analysis only traces of $BaCuO_2$ are present as an impurity phase in these two Cr-substituted $YBa_2Cu_4O_8$ samples. However, peak intensities of the impurity phases increased with further enhanced Cr content. Moreover, a minor amount of Y-123 phase could be additionally detected in the XRD pattern of the $YBa_2(Cu_{0.9}Cr_{0.1})_4O_8$ cuprate. On further increasing the substitution level, the main peaks in the XRD patterns of these samples can be attributed to the impurity phases (Y-123 and Y-247). Starting from 20% substitution, characteristic features of the orthorhombic Y-124 diffraction pattern already vanish: the intensities of the (113) and (108) reflections at $2\theta\cong34.4$ and 35.8° decrease strongly and the splitting of the (200), (020), (0014) at $2\theta\cong47°$ and the (017), (111) diffractions at $2\theta\cong33°$ vanishes. These results clearly show that in the case of x=0.20, peaks due to the Y-124 phase have altogether disappeared.

Conclusions

Cr-substituted $YBa_2(Cu_{1-x}Cr_x)_4O_8$ samples were synthesized by a simple aqueous sol–gel method. Y–Ba–Cu(Cr)–O acetate–tartrate gels, the products after intermediate calcination of precursor gels at 700°C and the end products obtained at 800°C were characterized by TG/DTA methods, powder X-ray diffraction analysis and resistivity measurements. Thermal characterization of the gel samples gave valuable information about the mechanisms of thermal decomposition of the precursors and the optimum conditions for the solid-state reaction to obtain superconducting samples. According to the thermogravimetric data the optimum annealing temperature for the preparation of Y-124 oxide was determined. We have demonstrated that Y-124 phase did not form after calcination of gels at 700°C. Annealing at this temperature produced a wide variety of different oxide, carbonate and oxycarbonate phases. The phase purity of the $YBa_2(Cu_{1-x}Cr_x)_4O_8$ samples synthesized at 800°C was checked by TG measurements in air. The TG curves for the $YBa_2(Cu_{0.99}Cr_{0.01})_4O_8$, $YBa_2(Cu_{0.97}Cr_{0.03})_4O_8$ and $YBa_2(Cu_{0.95}Cr_{0.05})_4O_8$ samples showed no mass loss below ~800°C indicating that these three samples mainly contain the pure Y-124 phase. However, for the samples with higher amount of chromium ($YBa_2(Cu_{0.9}Cr_{0.1})_4O_8$ and $YBa_2(Cu_{0.8}Cr_{0.2})_4O_8$) an additional mass loss around 400–500°C was detected. Such observation confirmed the possible formation of $YBa_2Cu_3O_{7-\delta}$ and $Y_2Ba_4Cu_7O_{15}$ phases in these samples. It was also demonstrated, that the critical temperature of superconductivity in $YBa_2(Cu_{1-x}Cr_x)_4O_8$ cuprates decreases almost linearly with the increasing chromium substitutional level. In conclusion, the results obtained here demonstrate, that TG/DTA analysis is an indispensable tool in order to establish the experimental details for the preparation of ceramic materials, including high-temperature superconductors.

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