

EFFECT OF GRINDING OF Y_2O_3 , $BaCO_3$ AND CuO ON SYNTHESIS OF $YBa_2Cu_3O_7$

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Received July 12, 1996.

The very fine and surface reactive powder mixture was prepared by highly intensive short time mill grinding of the components Y_2O_3 , $BaCO_3$ and CuO . Pure $YBa_2Cu_3O_7$ created by reaction of the components of grinding mixture at temperature 900 - 950 °C. The temperature of the synthesis of $YBa_2Cu_3O_7$ decreased owing to the grinding about 50 to 100 °C. Lower temperature of the synthesis had a positive effect on the purity of the final product.

INTRODUCTION

Production of supraconductive ceramic materials is based on the preparation of the very fine and high-purity powder precursors [1-6]. Preparation of the precursors involves calcination of the perfectly dispersed homogeneous mixture of powders of the defined stoichiometry. The particles size of initial powders is required to be under 1 micrometer because high calcination temperatures favour the growth of crystals. Powders of the Y-Ba-Cu-O system undergo calcination at 800 to 950 °C and are sintered at temperatures below 980 °C in controlled oxygen atmosphere in order to obtain the required supraconductive orthorhombic phase $YBa_2Cu_3O_{7-x}$. The product is thermally unstable above the temperature of the sintering.

Effect of grinding on the process of calcination and on the synthesis of supraconductive phases was studied in papers [3-9]. Awano M. et.al.[3] and Suamoro S. et al.[7] showed that the homogenization and mill grinding techniques of powders has a significant influence on the formation of new phases during heat treatment. More intensive homogenizing mixture formed the phases in the Y-Ba-Cu-O system like $YBa_2Cu_3O_{7-x}$, $Y_2Cu_2O_5$, $BaCuO_2$, BaY_2CuO_5 and others at lower temperature. Daturi M. et.al. [8] succeeded the partial mechanochemical synthesis by grinding of the mixture Y_2O_3 , $BaCO_3$ and CuO in the mill Spex-Mixed-Mill Model 8000 in argon gas. The grain size of the powders decreased with the prolongation of grinding accompanied by the degradation of crystallinity. After 100 hours of grinding appeared the new phase of $Y_2Cu_2O_5$. Ryu H. et al.[4] and Awano et.al.[3,9] studied the dependence of the intensive pregrinding of the reaction mixture powders on the superconductive

characteristics of ceramics. The short term grinding very positively affects the increase of critical current density of sintered bodies. The longer grinding of the powder does not always favourably affect the required characteristics final materials.

The effects of intensive pregrinding of the reaction mixture has been described in [10,11]. The solid state synthesis that takes place during grinding is attributed to the disturbances in the structure of the reacting components and their partial conversion. The nuclei of the product as the structural defects represent the loci of the concentration of elastic stress and provide the centres of nucleation for the subsequent thermally activated stage. When the particle size decreases and the surface activity of particles increases and the agglomerates are formed then the rate of surface diffusion during sintering grows. The result of this is often the lowering of the temperature of synthesis in the solid phase systems by as much as 100 to 200 K which can be accompanied by improved target properties of the final material.

The object of this paper is - to prepare a powder which after calcination exhibits a high proportion of the $YBa_2Cu_3O_{7-x}$ by highly intensive short time grinding; - to determine the effect of grinding on the reactivity of the homogeneous mixture of Y_2O_3 , $BaCO_3$ and CuO at heat treatment, the lowering the temperature, the accelerating of synthesis and its completion within shorter times in order to reduce the crystal growth.

EXPERIMENTAL PART

Powders of Y_2O_3 , $BaCO_3$ and CuO used for experiments were of p.a. purity and the following specific surface areas: Y_2O_3 : $S_A = 2.8155 \text{ m}^2 \text{ g}^{-1}$, $BaCO_3$: $S_A =$

$= 3.2553 \text{ m}^2 \text{ g}^{-1}$, $\text{CuO} : S_A = 0.9546 \text{ m}^2 \text{ g}^{-1}$. The mixed powder with the mole ratio $\text{Y}_2\text{O}_3 : \text{BaCO}_3 : \text{CuO} = 0.5 : 2 : 3$ were homogenized. The specific surface area of the mixture was $2.0260 - 1.9746 \text{ m}^2 \text{ g}^{-1}$. The distribution of particle size of the mixed powder is given by curve 0 min in figure 1. This mixture was ground in a planetary mill AGO-2 (U.R.S. Technology Com.Budakeszi, Hungary) at the following parameters of grinding: number of revolutions 760 min^{-1} , number of compartments 2 (with sillon inner surface layer, internal volume 60 cm^3), grinding tools-cylinders of ZrO_2 (radius 10 mm, length 10 mm), total weight of the grinding tools 70 g. 15 grams of the mixture was ground compartment during 2 to 120 minutes.

The surface area of the powders was determined by GEMINI 2360 (fy Micromeritics, USA). Measurements and calculations are related to the B.E.T method. The distribution of the particle size was determined on Sympatec HELOS-particle size analysis (fy Sympatec GmbH, Clausthal - Zeller, Deutschland) in the air flow (i.g. by dry method). The data were processed by computer program RODOS.

Thermal analysis of the samples was carried out on SETARAM unit TGA 92 (Société d'Etudes d'Automatisation de Regulation et d'Appareils des Mesures, France) under the following conditions: heating - heating rate $10^\circ\text{C min}^{-1}$ to temperature 970°C and 50 minutes of maintaining at the highest temperature; atmosphere - air; the sample weight 30 - 90 mg.

X-ray diffraction measurements were carried out using an automatic SIEMENS D500 diffractometer controlled by an AUTOCOMPT computerizing DIFRACT-AT software and an ICCD-JCPDS database. Vertical divergence of X-ray beam ($\text{FeK}\alpha$ radiation) was restricted using two Soller's diaphragms. Measurements were carried out in a vacuum of 0.2 Pa. Samples were measured on a platinum support which was heated to temperatures of 293-1273 K with the accuracy $\pm 5 \text{ K}$ [12]. After heating the sample to the selected temperature, the individual diffraction lines were taken in relatively short time intervals (8 minutes). Repeated measurements of the intensities of individual diffraction lines were stopped when the difference between the intensities measured in two consecutive steps was not apparent. This procedure took approximately 45 minutes at each temperature. Then the diffraction pattern was taken at the given temperature and this took 4 hours at each temperature.

RESULTS AND DISCUSSION

Particle size of the powder mixture Y_2O_3 , BaCO_3 and CuO that was ground in AGO -2 mill significant decreased and specific surface sharp increased at an first stage of grinding (figures 1 and 2). The curves 2 min.

and 5 min. shown in figure 1 already prove the formation agglomerates. The increase in the surface activity of the components results in their subsequent aggregation. The shape of the curve in figure 2 suggests that within 5 to 60 minutes of grinding the particle size of the material decreases accompanied by the formation of agglomerates. The created close contacts between reactants are the points suitable for initiation of the surface reaction. We studied the reactivities the samples ground for 60 and 120 minutes and compared them with the reactivity of the initial sample before grinding.

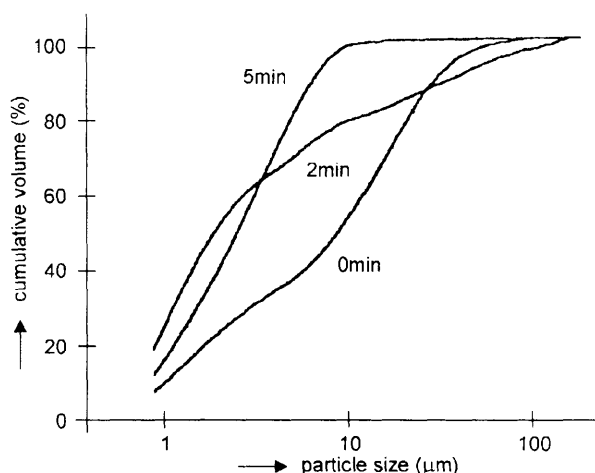


Figure 1. Particle size analysis of the powder mixture $\text{Y}_2\text{O}_3 + \text{BaCO}_3 + \text{CuO}$.

0 min - prior to grinding; 2 min - after 2 minutes of grinding; 5 min - after 5 minutes of grinding in AGO-2 mill

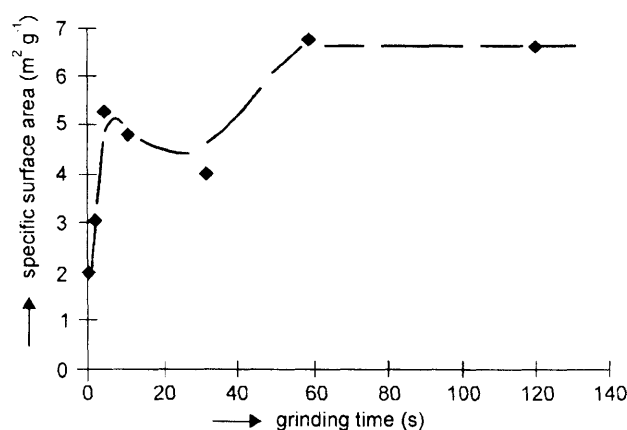


Figure 2. Evolution of the specific surface area of the $\text{Y}_2\text{O}_3 + \text{BaCO}_3 + \text{CuO}$ mixture with time of grinding.

The X-ray diffraction patterns of the initial sample before grinding and the patterns of the ground samples obtained at room temperature have different intensity of peaks. The intensities of individual peaks of the initial mixture correspond with the relative amount of the initial components in the mixture. Intensities of the peaks decreased by one half as a result of grinding in samples ground for 60 minutes whereas after 120 minutes of grinding dropped to one third in comparison with the initial sample. This remarkable decrease in intensities of the major peaks with the grinding time is attributed to the decrease in the size crystallites that can lead to amorphous state of the initial components.

Thermal expansion of the lattices of individual components results in minor shifts of the location of the peaks on the X-ray diffraction patterns. Diffraction patterns of the samples have remained almost unchanged on heating to 750 °C. In the initial sample (figure 3) transformation of the initial gamma modification of $BaCO_3$ to beta $BaCO_3$ took place in the temperature range 800 to 900 °C. The newly appeared peaks were at-

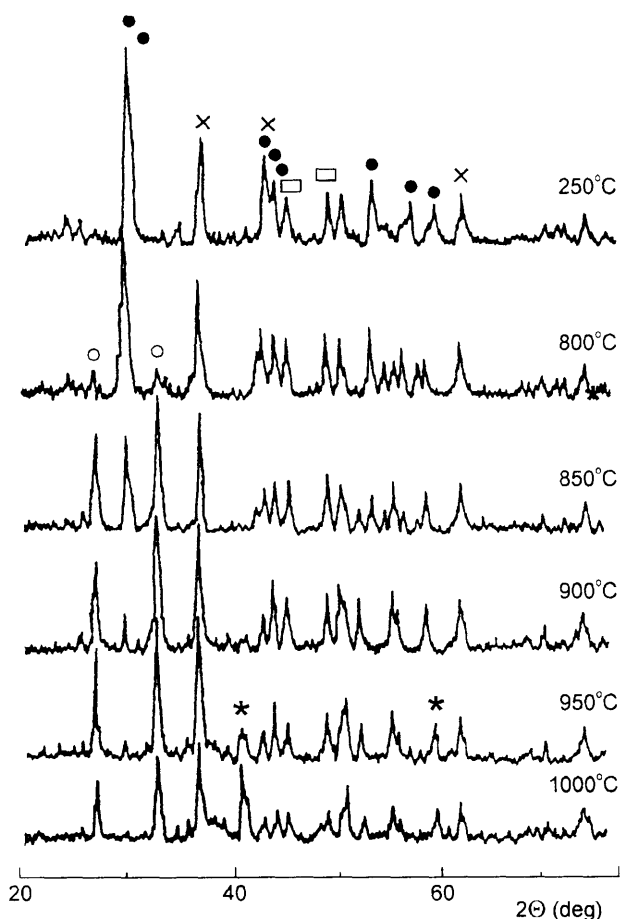


Figure 3. X-ray diffraction patterns of the powder mixture $Y_2O_3 + BaCO_3 + CuO$ prior to grinding at temperatures of 250, 800, 850, 900, 950 and 1000 °C.

□ - CuO , × - Y_2O_3 , ● - γ - $BaCO_3$, ○ - β - $BaCO_3$, * - $YBa_2Cu_3O_7$

tributed to β - $BaCO_3$ in accordance with the RIFRAN diffraction pattern evaluation system [13]. The disappearance of the peaks of β - $BaCO_3$ was observed above 900 °C together with the appearance of characteristic peaks of the phase $YBa_2Cu_3O_7$ (1237). The crystalline phase $YBa_2Cu_3O_7$ was reliably identifiable only above 950 °C. After 3 hours of holding time at 1000 °C the peaks of this phase reached maximum. Alongside with this prevailing crystalline phase other peaks were found that were attributed to $Ba_2Y_2O_5$, $BaCuY_2O_5$ and $BaCuO_2$. Diffraction pattern obtained after 4 hours holding time at 1000 °C confirmed that phase 1237 undergoes decomposition, the amounts the above mentioned compounds and others unidentified phases increased.

The disappearance of the primary crystalline phases is much faster and more intensive in ground samples (figures 4,5). New phases appeared at temperatures lower

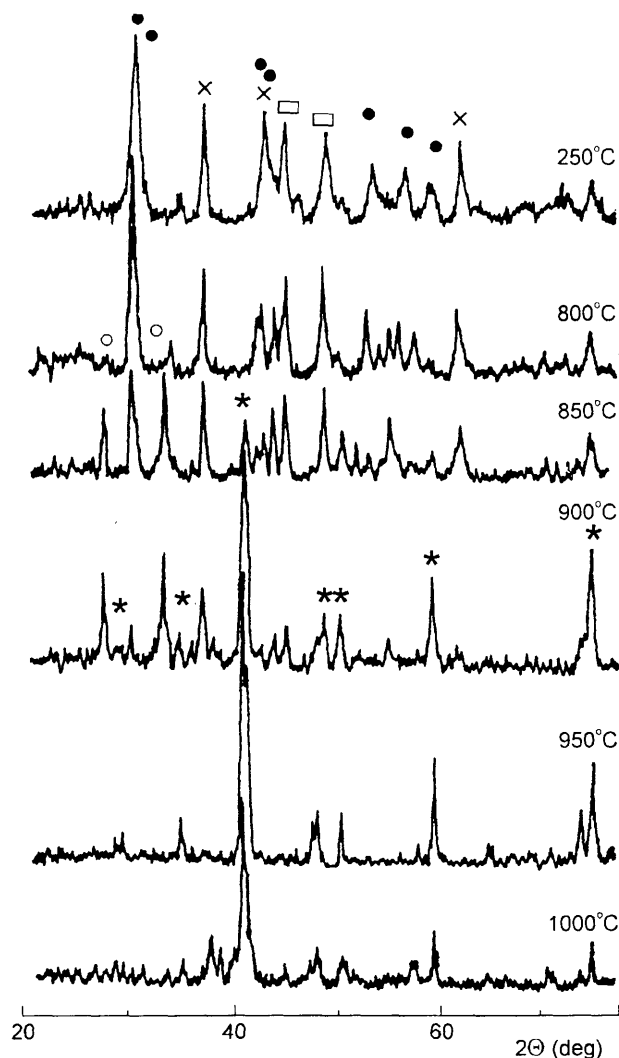


Figure 4. X-ray diffraction patterns of $Y_2O_3 + BaCO_3 + CuO$ powder sample ground for 60 minutes at temperatures of 250, 800, 850, 900, 950 and 1000 °C.

□ - CuO , × - Y_2O_3 , ● - γ - $BaCO_3$, ○ - β - $BaCO_3$, * - $YBa_2Cu_3O_7$

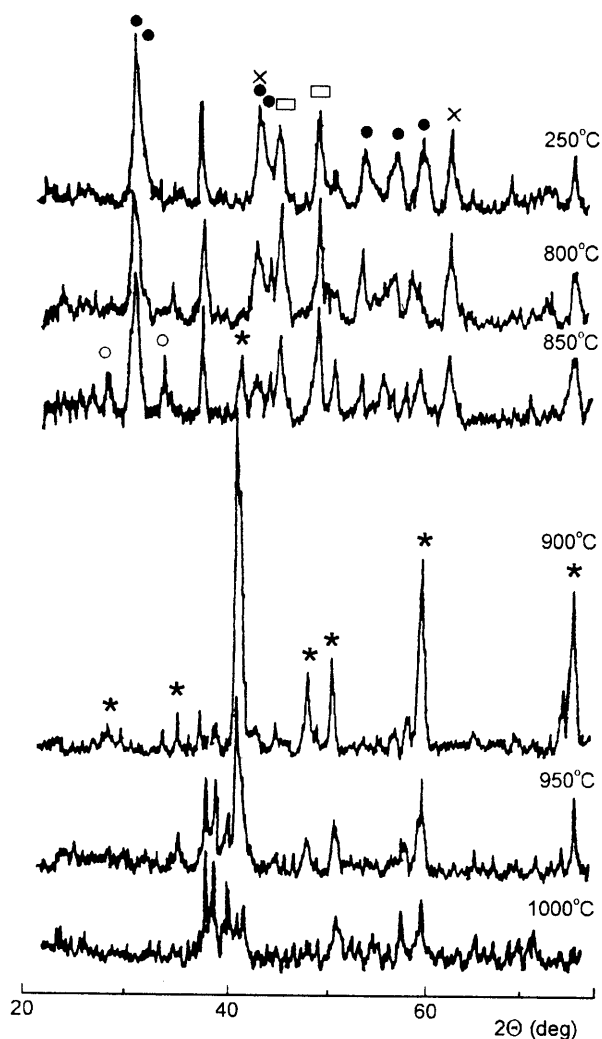


Figure 5. X-ray diffraction pattern of the sample of mixed powders $\text{Y}_2\text{O}_3 + \text{BaCO}_3 + \text{CuO}$ ground for 120 minutes at temperatures 250, 700, 800, 900, 950 and 1000°C.

□ - CuO , × - Y_2O_3 , ● - γ - BaCO_3 ; ○ - β - BaCO_3 ; * - $\text{YBa}_2\text{Cu}_3\text{O}_7$

by approx. 50 °C. The phase transformation γ - to β - BaCO_3 at about 800 °C again preceded the formation of $\text{YBa}_2\text{Cu}_3\text{O}_7$ phase. Sample ground for 60 minutes had on its diffraction pattern pure phase 1237 at 950 °C and sample ground for 120 minutes at 900 °C. At 1000 °C the decomposition of phase 1237 was more obvious in the sample ground for 120 minutes. Its x-ray diffraction pattern has become unclear due to large number of phases of newly created mixed oxides.

S. Suasmoro et al.[7] reported similar results. Mixtures of Y_2O_3 , BaCO_3 and CuO were ground by various methods and studied by DTA. First endothermic effect at 815 °C was attributed γ to β transformation of BaCO_3 ,

next effects the synthesis $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ phases. Mixtures that underwent more intensive grinding contained higher proportion of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ phase after 6 hours calcination at 875 °C.

Thermogravimetric curves of the initial mixture and of the samples ground for 30, 60 and 120 minutes, plotted in figure 6 indicate the increasing reactivity of the surface with the time of grinding. Samples that were ground for 30, 60 and 120 minutes lost below 400 °C 1.6, 3.5 and 6 wt.% of their weight, respectively. Probably, the increased reactivity results from the creation of new surface and from the formation of structural defects in the crystalline lattice on the surface of grains that have significant concentration in intensively ground samples. The part of energy grinding is accumulated in the structural defects.

The total weight loss of the no-grinding sample after it has been held at 970 °C for 50 minutes was 7.5 wt.%. The weight losses of the ground samples above 850 °C after 50 minutes of holding at 970 °C of the samples that had been ground for 30 and 120 minutes were approx. 11 and 8 wt.% respectively.

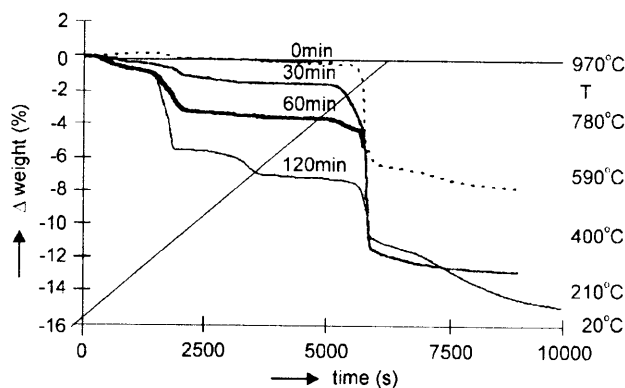


Figure 6. Curves of thermogravimetric analysis of the mixed powder $\text{Y}_2\text{O}_3 + \text{BaCO}_3 + \text{CuO}$ prior to grinding (0 min) and of the mixtures ground in AGO 2 mill for 30, 60 and 120 minutes.

Barium carbonate decomposes in consequence of its interaction with oxides present in the mixture at higher temperatures, mainly after its transformation from γ to β modification. 11.8 wt.% is the theoretical weight loss for the elimination CO_2 from the tested mixture of $\text{Y}_2\text{O}_3 + \text{BaCO}_3 + \text{CuO}$. The weight loss of the 30 minutes ground sample at temperature above 850 °C roughly corresponds with the theoretical value. Therefore we suppose, the weight loss at temperature below 300 °C is due to desorption of water or gases that had been adsorbed on the surface of the ground powders from the air. However we cannot neglect increased weight losses observed on the TG curves that had been detected in the more mechanically activated samples at temperatures

around 300-400 °C and in the most activated sample at temperatures around 500 °C. As a result of the structural defects in the crystals created by grinding the partial conversion of the carbonates could take place at heating, i.e. it could either interact with the oxides accompanied by partial liberation of carbon dioxide or it could undergo local thermal decomposition of the highly defective portions of grained $BaCO_3$. Nuclei of new components with poorly developed structures cannot be due to their small amounts identified by X-ray diffraction. Escaping gaseous component could be analyzed by mass spectrometry and it might prove the weightless observed at lower temperatures.

CONCLUSION

Mill grinding of the powder mixture of Y_2O_3 + $BaCO_3$ + CuO in a planetary mill AGO-2 had positive effect on the pure of product $YBa_2Cu_3O_7$ formed by heat treatment, lowered the temperature of synthesis of this phases about 50 - 100 °C and speeded up the form of the new phases. $YBa_2Cu_3O_7$ was the only one detected in samples ground for 60 and 120 minutes at temperature 950 and 900 °C respectively. This is the result of the perfect homogeneity, fine-graininess, the large specific surface area and high surface reactivity of the ground sample.

By X-ray diffraction was not proved mechanochemical synthesis even in the most mechanically activated sample.

Synthesis of $YBa_2Cu_3O_7$ from the unground mixture of Y_2O_3 , $BaCO_3$ and CuO was substantially slower even at 1000 °C. After 3 hours holding at 1000 °C other mixed oxides of Y, Ba and Cu were detected along side the predominant phase 1237. Their relative amounts increased with the holding time at the expense of the amount of $YBa_2Cu_3O_7$.

Acknowledgment

The authors would like to express their sincere gratitude to Ing. M. Škrobán from the Faculty of Metallurgy for his helpful comments and contribution to the interpretations of the x-ray diffraction patterns.

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Submitted in English by the authors.

EFEKT MLETIA ZMESI Y_2O_3 , $BaCO_3$ A CuO NA SYNTÉZU $YBa_2Cu_3O_7$

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Príprava supravodivých materiálov vychádza z jemných práškových prekurzorov, ktoré sú najčastejšie pripravené chemickou cestou. Prekurzor predstavuje ultrajemnú zmes oxidov. Zastúpenie nosných oxidov odpovedá stechiometrii žiadanej konečnej fázy. Zmes vhodná pre prípravu supravodičov sa dá pripraviť aj mletím [1-6].

Výsledky štúdia mechanicky aktivovaných sústav [10,11] ukázali, že mletím s rastúcou jemnosťou a povrchovou aktivitou častíc rastie hutnosť aglomerátov a rýchlosť povrchovej difúzie pri spekaní. Dôsledkom toho je často pozorované zníženie teplôt syntézy v tuhofázových systémoch o 100 až 200 K, ktoré môže byť sprevádzané aj zlepšením cieľových vlastností materiálov.

Za účelom zníženia teploty syntézy $YBa_2Cu_3O_7$, bol sledovaný efekt vysokointenzívneho mletia zmesi Y_2O_3 , $BaCO_3$ a CuO . Záznamy rgt - difrakčných analýz (s postupným ohrevom do teplôt 1273 K) nemletej - referenčnej vzorky a mletých vzoriek ukázali (obr.3,4,5), že žiadaná sledovaná fáza sa tvorí nad teplotou 800°C a že je termicky nestabilná. Vzniku $YBa_2Cu_3O_7$ predchádzala pri teplote nad 800°C transformačná

premena z γ -BaCO₃ na formu β -BaCO₃. Vysokointenzívne mletie (dokonalé zhomogenizovanie, zväčšenie povrchu látok, vytváranie aglomerátov, ktoré sa s časom mletia zhutňujú a porušenie kryštalickej štruktúry) na planetárnom mlyne AGO-2 viedlo k syntéze YBa₂Cu₃O₇ pri teplotách o 50 až 100°C nižších ako v prípade nemletej vzorky. Fáza YBa₂Cu₃O₇ bola identifikovaná ako jediná kryštalická fáza pri teplote 950°C u vzorky mletej 60 min. a pri 900°C u vzorky mletej 120 min. U nemletej vzorky boli pri teplote 950°C identifikované len dva malé píky charakteristické pre fázu YBa₂Cu₃O₇. Počas 3 hod. temperácie pri 1000°C ich intenzita rástla, ale zároveň sa objavoval rad nových píkov prínáležiacich novým oxidickým zlúčeninám yttria, bária a medi. Rovnako termicky nestabilné boli aj mleté vzorky nad teplotou 950°C.

Vplyv mletia na parciálny rozklad BaCO₃ nebol jednoznačne dokázaný. Porovnaním TG záznamov testovaných vzoriek (obr.6) sa ukázalo, že reaktivita s časom mletia rastie. Na čerstvý štruktúrne porušený povrch sa pravdepodobne viaže zo vzduchu voda, ktorá sa uvoľňuje pri ohreve do 350°C. Za percentuálny úbytok hmotnosti v okolí 400-500°C vzorky mletej 120 min. by mohol byť aj zodpovedný parciálny rozklad karbonátu. Toto množstvo pevných produktov rozkladu by nebolo detekovateľné rtg - analýzou aj keby sa jednalo o dokonale kryštalickú fázu. Podporiť tvrdenie, že dochádza k parciálnemu rozkladu karbonátu, podmieneného prípadne aj interakciou s ostatnými zložkami zmesi, by mohla len hmotnostná spektrometrická analýza plynov uvoľňovaných počas gravimetrickej analýzy.