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DTA AND CHEMICAL CHARACTERISTICS OF $YBa_2Cu_3O_{6.5+\gamma}$ SUPERCONDUCTOR PROCESSING FROM DIFFERENT RAW MATERIALS

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The Y:Ba:Cu = 1:2:3 coprecipitates of carbonates (precipitated with Na_2CO_3 or Na_2CO_3–NaOH solution) and of oxalates (obtained in aqueous, partly aqueous and non-aqueous media) were investigated as concerns the yield and stoichiometry of the precipitates, including their transmission electron microscopy and DTA characteristics. Oxalates coprecipitated from acetate solutions in non-aqueous media provide fine samples with increased reactivity. For comparison, when thermally treated, an oxide ceramic mixture containing aged BaO (with some $Ba(OH)_2$ and BaO_2) exhibits increased reactivity due to the formation of a liquid phase in the temperature range 400–500°.

Numerous studies have been published to describe various characteristics of superconductive $YBa_2Cu_3O_{6'5+y}$. In most cases, the starting material is a mechanical, well-homogenized mixture of $BaCO_3$, Y_2O_3 and CuO (as also used in our previous studies [1]). It is obvious that the desired solid-state reactions occur at increased temperatures, above 850°. Such high temperatures are favourable for the attainment of homogeneity and a high content of the $YBa_2Cu_3O_{6.5+y}$ phase, but deteriorate the oxygen nonstoichiometry (y), consequently requiring that the material be annealed in an oxygen atmosphere at lower temperatures to ensure its superconductivity. Therefore, it is of interest to look for a chemical procedure which would increase the reactivity of the starting material. For example, in the above-mentioned mixture, $BaCO_3$ can be replaced by $Ba(OH)_2$ or BaO_2, which form a liquid phase in the temperature range 400–450°, enhancing the low-temperature reactivity.

Coprecipitation of insoluble metal salts appears to be a promising method for obtaining intimate solid mixtures. One can assume that carbonate and/or oxalate coprecipitates of the three metal (Y, Ba and Cu) may be favourable starting materials for the mixed oxides; moreover, decomposition of the mixed oxalates can

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be expected to provide oxides with higher reactivity. Attaining the required stoichiometry and high purity of such coprecipitates seems to be the critical problem of these "wet" methods of preparation. The aim of this contribution is to determine the chemical characteristics and thermal behaviour of some carbonate and oxalate coprecipitates with an assumed Y : Ba : Cu ratio of 1 : 2 : 3, and to compare them with those obtained by ordinary mixing of Y_2O_3, BaO and CuO.

Results and discussion

The major sample characteristics are listed in Table 1. It can be seen from Fig. 1 : 1 and 1 : 2 that the products of carbonate peecipitations both in neutral (sample 2) and in alkaline (sample 4) media are clearly mixtures of different types of particles, which can be assigned to the individual carbonates of the three metals. The coprecipitation reaction of Y, Ba and Cu nitrates with carbonate appears to be quantitative. The sample contained minor amounts of sodium (0.18% and 0.38% for samples 2 and 4, respectively) from the precipitating agent.

Studies have been performed in which the starting material was made by oxalate coprecipitation, i.e. addition of oxalic acid solution to a solution containing the nitrates of Y, Ba and Cu in the required atomic ratio of 1 : 2 : 3. It was not explicitly stated that the initial ratio of metals in the solution corresponded to that of the coprecipitate obtained, and nor was any chemical analysis reported to confirm the stoichiometry of the latter. Because of both a low yield and a loss of barium, we did not attain any satisfactory results by applying the above-mentioned "simple" coprecipitation in acid aqueous media (sample 3, Table 1). Thus, we decided to investigate the conditions of oxalate formation in more detail to be published separately [2]. Here, we present the most significant examples of the coprecipitation in partly aqueous and in non-aqueous media. As shown by the product yield and stoichiometry (samples 7 and 13, Table 1), these methods are superior to that in aqueous media. It is of interest that the lower yield of the nitrate reaction as compared to that of the acetate reaction did not have any significant effect on the product stoichiometry. The morphological uniformity of the oxalate precipitates is also much better than that of the carbonate precipitates, as demonstrated by TEM (Fig. 1 : 1 to 1 : 5).

The DTA curves of the coprecipitates described in Table 1 are shown in Fig. 2, together with the DTA record of a homogenized mixture of BaO, CuO and Y_2O_3 (sample 1 cf. Fig. 1 : 6) in the required stoichiometric ratio. Chemical analysis of the active BaO content of aged barium oxide showed it to be as low as 70%, due to the absorbed components such as H_2O and CO_2. These impurities are first manifested by massive endothermic reactions; the three coupled endothermic peaks represent

Table 1 Condition of coprecipitation of carbonates and oxalates for initial composition Y : Ba : Cu = 1 : 2 : 3

Initial salt	Precipitate	Precipitating				Yield	Final composition			Sample
		agent	medium	p_H	temperature		Y	Ba	Cu	
Nitrates	carbonates	$NaHCO_3$	H_2O	5.5	20 °C	101 %	1	2.01	2.96	2
Nitrates	hydroxycarbonates	Na_2CO_3+ $+NaOH$	H_2O	11.5	20 °C	≅100 %	1	2.08	3.06	4
Nitrates	oxalates	$H_2C_2O_4$	H_2O	1.0	0 °C	82.6%	1	0.61	3.05	3
Nitrates	oxalates	$H_2C_2O_4$	H_2O+ $+C_2H_5OH$	—	0 °C	87.9%	1	2.05	3.09	7
Acetates	oxalates	$H_2C_2O_4$	C_2H_5OH	—	20 °C	94.3%	1	2.04	2.95	13

Initial concentration of Y^{3+} was $2.4 \cdot 10^{-2}$ mol l^{-1} and the total initial volume was 900 ml.

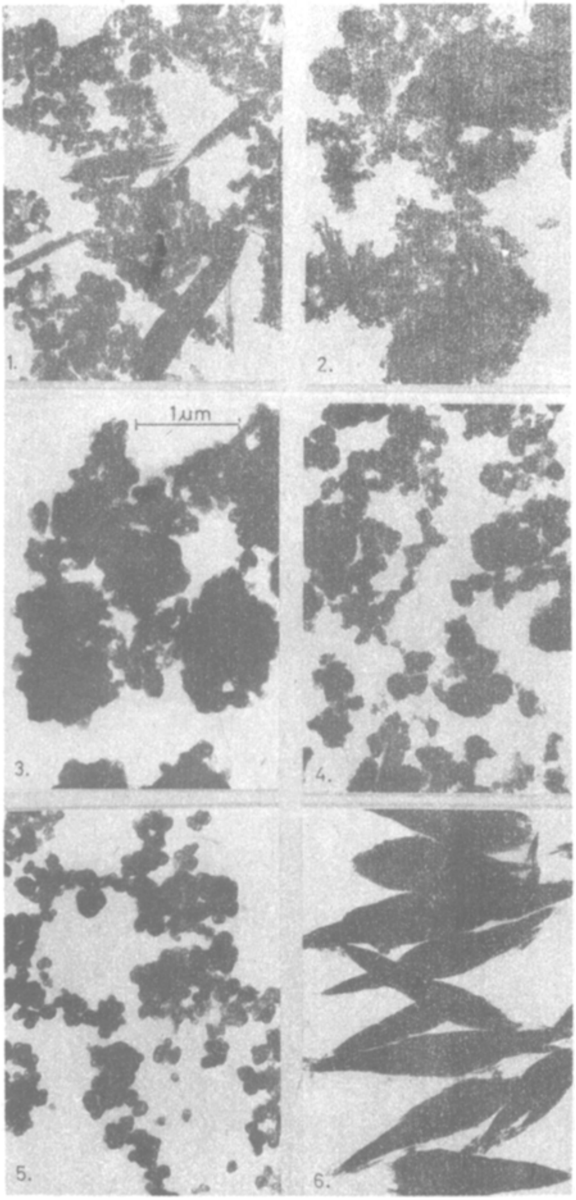

Fig. 1 Transmission electron microscopic pictures of samples 2 (1 : 1), 4 (1 : 2), 3 (1 : 3), 7 (1 : 4) and 13 (1 : 5) listed in Table 1, together with that of the homogenized starting mixture of oxides Y_2O_3, BaO and CuO, sample 1 (1 : 6)

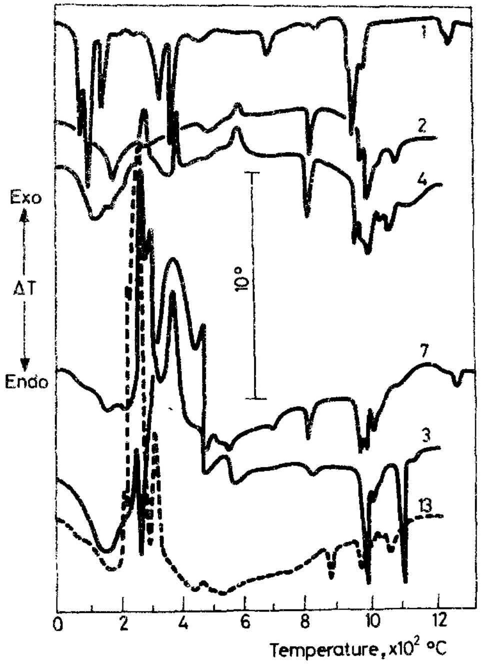

Fig. 2 Differential thermal analysis curves of the samples illustrated in Fig. 1 (cf. Table 1). Netzsch DTA apparatus equipped with separate Pt cells placed on top of the supporting corundum rods. Temperature measured with separate thermocouple and the measuring head calibrated with ICTA/NBS standard, using Al_2O_3 as reference material. As-received samples of precipitates (2, 4, 3, 7 and 13) and the mechanical mixture (1) of about 150 mg were heated in a stream of oxygen at a heating rate of 5 deg min^{-1}

dehydration and possibly melting of $Ba(OH)_2 \cdot 8H_2O$ at 78°. The following two endothermic peaks within the interval 300–400° possibly represent melting of $Ba(OH)_2$ and BaO_2. The presence of a liquid phase can considerably facilitate solid-state reactions, yielding the endothermic peak at 653°, possibly associated with oxygen release and resulting resolidification of the mixture. The endotherms starting at 920° possibly represent cooperative reactions of eutectic melting and decomposition of the 1 : 2 : 3 phase. A detailed analysis of the thermal behaviour of $YBa_2Cu_3O_{6.5+y}$ is the subject of another paper [3].

When this pattern is compared with that of the carbonate coprecipitate (the thermal behaviour of which can resemble that of the ordinary ceramic mixtures containing carbonates, curves 2 and 4), the lowered reactivity of the latter is shown by a large endothermic peak at 810° for the transition of $BaCO_3$ (serving as the internal temperature standard: ICTA recommendation). Further, the decomposition of the desired 1 : 2 : 3 phase is not presented, but other peaks at higher temperature (~1000°) are shown, indicating the decompositoon of unknown phases, including the $BaCO_3$ second polymorphic transition or the melting of $BaO \cdot BaCO_3$. For hydroxycarbonates (curve 4), two extra exothermic peaks can be observed in the range 200–400°, possibly associated with oxidation processes (e.g. $Cu^+ \rightarrow Cu^{2+}$) caused by the presence of atmospheric oxygen. Subsequent high-temperature peaks are again shifted to somewhat higher temperatures.

All three oxalates (curves 7, 3 and 13) show the cooperative thermal decomposition, which is exhibited as exothermic reactions due to the combustion of evolved carbon monoxide to carbon dioxide. In accordance with the particle size illustrated in Fig. 1:3 to 1:5, the width of the complex endothermic peaks gradually becomes narrowed from sample 3 to samples 7 and 13. The decreasing width and increasing sharpness of the exothermic peaks representing oxalate decomposition may reflect certain qualitative aspects of the increased reactivity of the resulting mixtures. Samples 3 and 7 show the endothermic peaks of the $BaCO_3$ transitions, while for sample 13 this is missing, but there is an additional endotherm at 877°, probably connected with a ternary eutectic melting, which is normally indicated for samples treated during the second DTA run [3]. The doubled peak of oxalate decomposition for sample 13 has an almost identical character to that of the record published by Ozawa et al. [4], who complemented their DTA studies with thermogravimetric data. Analysis of their weight loss data indicated the possible presence of oxyoxalates and hydroxyoxalates, which are probably responsible for the multi-tip occurrence of the DTA peaks of oxalate decomposition.

Conclusion

It follows that different methods of $YBa_2Cu_3O_{6.5+y}$ preparation may yield different products. DTA proved to be a useful tool for a quick quality control of the starting mixtures, inevitable for successful attainment of the desired properties.

References

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Zusammenfassung — Gemeinsam gefällte Carbonate (aus Na_2CO_3- bzw. Na_2CO_3–NAOH-Lösung) und Oxalate (aus wässeriger, wässerig-alkoholischer bzw. alkoholischer Lösung) von Y, Ba und Cu im Molverhältnis 1:2:3 wurden untersucht in Bezug auf die Ausbeute und Stöichiometrie der Fällungsprodukte, mittels Transmission-Elektronenmikroskopie und DTA. Durch Oxalatfällung aus Acetaten in nichtwässeriger Lösung wurden feinteilige Proben erhöhter Reaktivität erhalten. Zum Vergleich wurden oxidkeramische BaO-haltige Mischungen (die infolge Alterung durch $Ba(OH)_2$ und BaO_2 verunreinigt waren) thermisch behandelt und zeigten infolge Bildung einer flüssigen Phase im Temperaturbereich 400–500 °C ebenfalls erhöhte Reaktivität.

Резюме — Исследовано соосаждение карбонатов иттрия, бария и меди, взятых в соотношении 1:2:3 и полученных осаждением из растворов Na_2CO_3 или Na_2CO_3–NaOH, и оксалатов, получгнных в водной, частично водной и неводной средах. Изучен выход и стехиометрия осадков, их дифференциальный термический анализ и электронная микроскопия на пропускание. Оксалаты соосаждаются из растворов в неводной среде с образоением тонкоизмельченных образцов с большой реакционной способностью. После термической обработки оксидная керамическая смесь, содержащая состарившийся оксид бария с некоторой примесью $Ba(OH)_2$ и BaO_2, показывает увеличение реакционной способности, что обусловлено образованием жидкой фазы в области температур 400–500°.