Low-temperature synthesis route for YBa₂Cu₃O_x powder

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LOW-TEMPERATURE SYNTHESIS ROUTE FOR $\text{YBa}_2\text{Cu}_3\text{O}_x$ POWDER

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The preliminary results of a new low-temperature $\text{YBa}_2\text{Cu}_3\text{O}_x$ -powder preparation method are reported. The new method is based on the rapid decomposition at 750°C of a spray-dried (Y, Ba, Cu)-nitrate mixture. In this way a fine powder with a primary particle size of about $0.3\text{ }\mu\text{m}$ is obtained. A comparison is made with the conventional methods.

For ceramic processing generally a fine powder is required with a primary particle size of a few micrometer at most, preferably below $1\text{ }\mu\text{m}$. Only with such powders a small grain size can be obtained in the sintered product. The grain size plays an important role in the superconductive [1] and mechanical properties of the $\text{YBa}_2\text{Cu}_3\text{O}_x$ (123)-material. Especially with respect to microcracking phenomena a small grain size in the sintered material is essential [2].

The preparation route for 123-powder most frequently reported in the literature and also followed here, is a solid-state diffusion reaction starting with Y_2O_3 , CuO and BaCO_3 [3]. Instead of BaCO_3 , BaO_2 and $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ are also used. After mixing and firing in air at 950°C a sufficiently single-phase orthorhombic 123-powder results. This powder is coarse with primary particles of about $10\text{ }\mu\text{m}$, which form strong agglomerates of a size up to $100\text{ }\mu\text{m}$. Generally, growth of primary particles and agglomerates increases with calcination temperature due to sintering effects. It is therefore desirable to prepare 123-powder at a lower temperature.

A process step which is often used to lower the calcination temperature is spray-drying of ceramic precursors. In this way a high degree of mixing can be achieved. As precursors nitrates were chosen because they have relatively low decomposition tem-

peratures [4]. Moreover nitrates, in contrast to e.g. oxalates or citrates [5], cannot introduce carbonate or eventually carbon impurities which is undesirable for the sintering properties of the resulting powder. The solution to be spray-dried was obtained by adding aqueous $\text{Cu}(\text{NO}_3)_2$ and $\text{Ba}(\text{NO}_3)_2$ solutions in the appropriate ratios to a solution of Y_2O_3 in diluted nitric acid. The spray-dried light-green hygroscopic nitrate mixture was fired at temperatures between 750 and 900°C in air, with heating and cooling rates of 100 to $200^\circ\text{C}/\text{h}$. Sufficiently single phase 123-powder was not obtained within a few hours using this firing procedure. Moreover, the resulting powder was rather coarse with primary particles of about $10\text{ }\mu\text{m}$. At these temperatures this coarsening cannot be explained by sintering. Apparently there is another coarsening process. A possible explanation is that the occurrence of a molten $\text{Ba}(\text{NO}_3)_2$ phase at 600°C causes phase segregation and an increased primary particle size as a consequence. This coarsening process can successfully be prevented by rapid decomposition of the nitrate mixture. Moreover a fine grained orthorhombic 123-powder results. The process is described below.

A thin-walled silver crucible with a 3 mm thick layer of spray-dried 123-nitrate mixture was placed for a few minutes in an air-ventilated furnace preheated to about 750°C . Subsequently, the powders were air-quenched. X-ray analysis of the phase compositions after 0.5 , 1 , 2 , 4 , 8 and 16 minutes decomposition time revealed the reaction path as shown in

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fig. 1. From the figure can be seen that $\text{Ba}_3\text{Cu}_5\text{O}_x$ appears as an intermediate phase. Only small amounts of Y-containing phases were detected. These phases probably were amorphous, or had a very small particle size. Subsequently the Y-containing compounds reacted with the $\text{Ba}_3\text{Cu}_5\text{O}_x$ intermediate phase to form the 123-product. After a decomposition time of 8 minutes or longer, about 5 wt% of intermediate phases remained. This residual content is mainly determined by the thickness of the powder layer in the silver crucible. Thinner layers resulted in smaller amounts of intermediate phases. The powder which resulted after 8 minutes decomposition time had a primary particle size of about $0.3 \mu\text{m}$ and contained relatively weak agglomerates of 1 to $2 \mu\text{m}$ size. The powder was deagglomerated for 15 minutes in an agate ball-mill. After cold isostatic pressing at 4 kbar

Fig. 1. Reaction path of the formation of orthorhombic 123-compound by rapid 123-nitrate decomposition reactions at 750°C in flowing air. The residual intermediate phases are not indicated.

a relative density of 65% was obtained. By sintering in flowing O_2 at 950°C for 4 hours the relative density increased to 93%. Grain sizes of between 3 and $25 \mu\text{m}$ and rather elongated shapes were obtained. This morphology probably results from liquid phase sintering due to the presence of the $\text{Ba}_3\text{Cu}_5\text{O}_x$ compound [4]. The sintered samples showed a transition to zero resistivity at 90 K.

Resuming, it is shown that 123-powder can be prepared at 750°C , resulting in a much finer powder than the powders obtained by the conventional preparation routes. Two mechanisms account for the smaller particle size. At lower temperature considerably less sintering takes place and the rapid decomposition process prevents phase separation by a melting phase. It is desirable, however, to reduce the content of intermediate phases in the product and to even further reduce the formation of agglomerates. Therefore spray-roasting or fluid-bed decomposition of 123-nitrate mixtures seems to be a promising technique.

References

- [1] T.R. Dinger, to be published.
- [2] J.W. Severin and G. de With, Proc. Brit. Ceram. Soc. (1988), accepted for publication.
- [3] T. Kawai and M. Kanai, Jpn. J. Appl. Phys. 26(4) (1987) L736.
- [4] D.M. de Leeuw, C.A.H.A. Mutsaers, C. Langereis, H.C.A. Smoorenburg and P.J. Rommers, Physica C 152 (1988) 39.
- [5] B. Dunn, C.T. Chu, L-W Zhou, J.R. Cooper and G. Gruner, Adv. Ceram. Mater. 2 (1987) 343.