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SYNTHESIS OF OXIDE SUPERCONDUCTORS

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ABSTRACT

This paper briefly reviews recent study on synthesis of oxide superconductors by thermal analyses such as TG and TG-DTA.

INTRODUCTION

Since the first oxide superconductor was found by Sleight and his coworkers [1], research for superconductivity in oxides has been promoted and various oxide superconductors have been synthesized, particularly in the last few years after Tanaka and his colleagues [2] reconfirmed discovery of the oxide superconductor with the highest critical temperature by Bednorz and Muller [3]. Extensive works have been carried out, being further stimulated by discovery of the oxide superconductor with a critical temperature above liquid nitrogen temperature [4]. The oxide superconductors hitherto found in these extensive works are listed in Table 1.

Versatile applicability of thermal analysis was revealed in this research, and many techniques have been applied to various aspects of the research [12,13]. Measurements of electric resistivity and magnetic susceptibility with temperature change are, in essence, thermoanalytical techniques, i. e., thermoelectrometry (TE) and thermomagnetometry (TM). Observation of nonstoichiometry [12,14] and determination of oxygen content [12] by thermogravimetry (TG) are among the most important applications, because the oxygen content is closely related to superconductivity, and isotope effect on the critical temperature was observed by utilizing the oxygen nonstoichiometry. Differential scanning calorimetry (DSC) has a potential applicability; if a superconductor with the critical temperature above the low temperature limit of DSC is found, bulk superconductivity will be confirmed calorimetrically by DSC. Vapor pressure measurement by TG and evolved gas analysis or detection

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(EGA or EGD) is also important in development of the thin film technology, especially for molecular organic chemical vapor deposition. These applicabilities are summarized in Table 2.

Table 1 Oxide Superconductors

Materials	Critical Temperature	References
$La_{2-x}Ba_xCuO_4$	30 K	5, 6
$La_{2-x}Sr_xCuO_4$	40 - 50 K	5, 6
$YBa_2Cu_3O_{7-x}{}^*$	94 K	5, 6
$Bi_2Sr_2CuO_x$	30 - 40 K	7, 8
$Bi_2Sr_2CaCu_2O_x$	80 - 90 K	7, 8
$Bi_2Sr_2Ca_2Cu_3O_x$	110 - 120 K	7, 8
$Tl_2Ba_2CuO_x$	80 - 90 K	7
$Tl_2Ba_2CaCu_2O_x$	105 K	7
$Tl_2Ba_2Ca_2Cu_3O_x$	125 K	7
$TlBa_2CuO_5$	17 K	9
$TlBa_2CaCu_2O_7$	91 K	9
$TlBa_2Ca_2Cu_3O_9$	116 K	9
$TlBa_2Ca_3Cu_4O_{11}$	122 K	9
$(Tl,Pb)Sr_2CaCu_2O_x$	80 - 90 K	10
$(Tl,Pb)Sr_2Ca_2Cu_3O_x$	115 - 122 K	10
$Ba(Pb,Bi)O_3$	13 K	1
$(Ba,K)BiO_3$	30 K	11

* Y can be replaced by La, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb, and/or Lu.

For synthesis of the superconductors, various routes have been used, as shown in Fig. 1. Thermoanalytical techniques, such as TG and EGA, are very useful to observe these synthetic reactions accompanied by gas evolution and mass change. Differential thermal analysis (DTA) is also applied to observation of melting, glass formation and crystallization as well as the synthetic reactions, and these techniques provide us with useful information for synthesis and fabrication. The applications to synthesis are summarized in this report.

Table 2 Application of Thermal Analysis to Oxide Superconductors Research

Application fields	Techniques
Formation Process (+ Kinetics)	TG, DTA, EGA, MO*, ETA*
Crystalline Transition	DTA, TL*
Melting and Glass Formation	DTA, MO*
Oxygen Content	TG (TPR*), EGA
Nonstoichiometry	TG, EGA, (TL*)
Sintering and Crack Formation	TL
Thin Film Formation (Expansion Matching)	TL
Critical Temperature (T_C)	TE*, TM*, DSC?
Crystal Growth (Phase Diagram)	DTA
Vapor Pressure (MOCVD)	TG, EGA, EGD

MO: Microscopic Observation, ETA: Emanation Thermal Analysis
TL: Thermodilatometry, TPR: Temperature Programmed Reduction
TE: Thermoelectrometry, TM: Thermomagnetometry

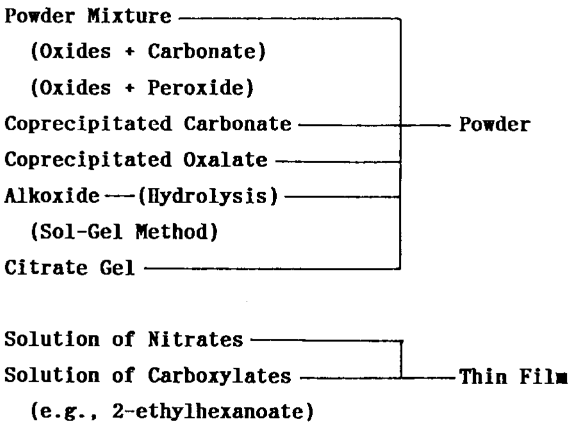

Fig. 1 Various Routes of Oxide Superconductor Synthesis

THERMAL ANALYSIS OF $YBa_2Cu_3O_{7-x}$ SYNTHESIS

Among many synthesis routes mentioned above, the synthesis from the powder mixture of $BaCO_3$, Y_2O_3, and CuO has been most widely used. According to numerous TG-DTA data reported on this process [15], the following general features appear in the TG-DTA curves:

(1) mass loss which begins to occur gradually at around 750 °C, and reaches almost constant at temperatures as high as 950 °C,

(2) an endothermic peak at 810 °C,

(3) an endothermic peak above 935 °C - 975 °C.

The mass loss is mostly due to CO_2 evolution from $BaCO_3$ during the perovskite formation and partly due to oxygen loss from the superconductor synthesized at higher temperatures. For this perovskite formation process, TG at various heating rates was applied in order to estimate a necessary duration of the heat treatment. Isothermal TG [16] was also applied to investigate proper heat treatment conditions for obtaining the superconductors with high quality. Kaisersberger et al. [17] investigated the synthesis of $EuBa_2Cu_3O_{7-x}$ by TG.

The endothermic peak is due to a transition of unreacted $BaCO_3$. The superconductor with unreacted portion sometimes shows a small peak at the same temperature [14]. This endothermic peak thus could be used to evaluate the quality of the synthesized sample. The endothermic peak in a higher temperature region is recognized to be a partial melting, although the temperatures reported [14-16] are not always in good agreement with each other. Note that two-component reactions could take place together with the three-component perovskite formation in the similar temperature range [18]. Homogeneity and particle size of the starting materials are therefore essentially important to obtain good superconductors.

Use of BaO_2 instead of $BaCO_3$ as a starting material is also reported [19-21]. Beruto et al. [20] used TG to obtain proper heat treatment conditions on $Eu_2O_3/4BaO_2/6CuO$ and $Ho_2O_3/4BaO_2/6CuO$. In these cases, a liquid phase is formed by the melting of BaO_2 [21] and the mass loss due to oxygen evolution from BaO_2 starts at 500 and 700 °C, respectively. The TG curves show a plateau above 900 °C, and further mass loss occurs at higher temperatures. Beruto et al. [20] insisted that plateau temperature is an optimal heat treatment temperature; that of the Eu-based oxide is 20 K lower than that of the Ho-base oxide.

TG-DTA on other starting materials show that they first change to precursors which are intermediate products stable below 500 °C, and then the perovskite formation occurs. Figure 2[14] shows typical results of the TG-DTA study of thermal decomposition of the coprecipitated oxalate under oxygen flow.

A little mass loss (2 % of the initial sample mass) around 100 °C is presumably due to dehydration. Two stages of decomposition are observed in the temperature ranges 250 - 320 °C and 380 - 430 °C. These reactions are thermal decomposition of the oxalate; they are all exothermic reactions due to combustion of volatilized carbon monoxide to carbon dioxide. The precursor obtained by thermal decomposition from the coprecipitated oxalate is characterized by its amorphous structure consisting of $BaCO_3$ and oxides of yttrium and copper, although it's not clear whether or not $BaCO_3$, Y_2O_3, and CuO exist as pure components without atomic interactions; crystal growth of these materials proceeds with increasing temperature. The final stage of the mass loss is perovskite formation process accompanied by CO_2 evolution from $BaCO_3$. The CO_2 evolution has been reconfirmed from EGA study by Negishi et al. [22] and by Gustavo et al. [23]. Balek and Sestak [24] used emanation thermal analysis (ETA) to investigate synthesis from the coprecipitated oxalate. The ETA curve shows a few peaks reflecting stepwise microstructure changes during heating over a temperature range between 300 °C and 750 °C. The ETA thus can be used as a suitable tool for qualitative testing of the intermediate products of oxide superconductors.

TG-DTA curves for thermal decomposition of the coprecipitated carbonate [25] are quite similar to the coprecipitated oxalate. The precursor from the coprecipitated carbonate is also in amorphous state.

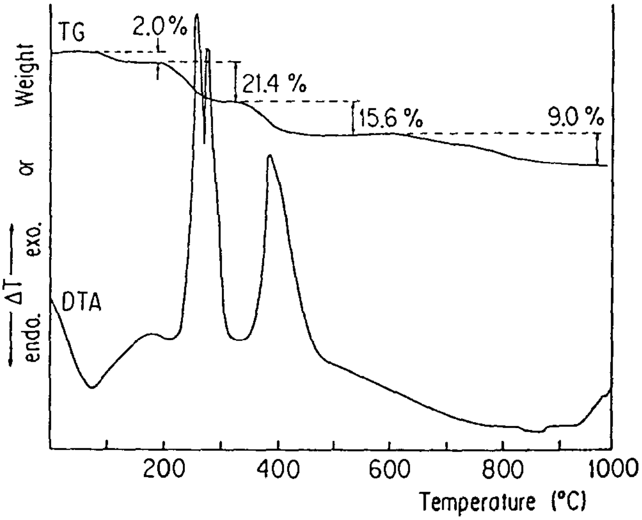

Fig. 2 Typical TG-DTA curve of thermal decomposition of coprecipitated oxalate

Chu and Dunn [26,27] investigated the preparation of the superconductor by the amorphous citrate process by TG and X-ray diffraction. In this process, individual nitrate solutions of barium, yttrium, and copper are mixed with citric acid, and then the amorphous solid is obtained by heating the solution at 75 ^{o}C and at 85 ^{o}C. The first stage of the mass loss around 300 ^{o}C is the decomposition of barium citrate complex, and $Ba(NO_3)_2$ and $BaCO_3$ are clearly evident just after the decomposition. In the second stage at around 400 ^{o}C, yttrium and copper oxides are formed, and usually barium nitrate phase is no longer present at 500 ^{o}C. Hirano et al. [28] proposed preparation of chemically homogeneous submicron powder of $YBa_2Cu_3O_{7-x}$ by partial hydrolysis of metal alkoxides. It was observed that the specimen prepared shows less-detectable mass loss above 600 ^{o}C in comparison with the specimen prepared without any water addition.

Among several thin-film preparation methods, TG has been most extensively applied to the synthesis from metal carboxylate precursors [29], particularly mixed solutions of 2-ethylhexanoates of barium, yttrium, and copper. TG-DTA curves of the mixed solutions are just the sum of the TG-DTA curves of the component solutions [29-31]. The mixed solutions are therefore decomposed to $BaCO_3$, Y_2O_3, and CuO below 400 ^{o}C. The precursor is also in amorphous state, although crystal growth seems to proceed in lower temperatures compared with the precursors from the coprecipitated oxalate and carbonate. Yokota et al. used TG for decomposition processes of several organic acid salts of barium [32], yttrium [33], and copper [34]. It is pointed out [33] that yttrium oxide formed by the decomposition of yttrium organic acid salts such as 2-ethylhexanoate is amorphous at 400 -500 ^{o}C and crystallized at 550 ^{o}C.

KINETICS OF $YBa_2Cu_3O_{7-x}$ FORMATION

As described above, $YBa_2Cu_3O_{7-x}$ is the most suitable substance for thermal analysis. One of the reasons is that reaction forming $YBa_2Cu_3O_{7-x}$ from different starting materials can be observed from its beginning to the completion by thermal analysis, so that kinetic analysis can be applied easily to thermoanalytical curves. Typical results of such kinetic analysis were reported in a series of papers [22,25,30] and their summarizing review was presented at the 9th ICTA Congress [35].

According to these reports, TG-DTA was applied to processes forming $YBa_2Cu_3O_{7-x}$ from coprecipitated oxalate, coprecipitated carbonate, solution mixture of 2-ethylhexanoates and powder mixture of $BaCO_3$, Y_2O_3, and CuO; a kinetic analysis method [36] was applied to the results of the final stage of thermal decomposition of precursors, and the following conclusions were derived.

(1) A single elementary reaction proceeds in the thermal decomposition of the precursors made from the coprecipitated oxalate, the coprecipitated carbonate and the mixture of 2-ethylhexanoates. However, multiple elementary reactions occur in the process forming $YBa_2Cu_3O_{7-x}$ from the powder mixture.

(2) For the processes consisting of the single elementary reaction, the activation energies were estimated; they are in the range from 263 kJ/mol to 282 kJ/mol.

(3) By using the activation energy, experimental master curves were obtained for the conversion versus the generalized time, i. e., the reduced time [36], on each reaction; the master curves can be used to predict the processes under temperature conditions different from TG.

(4) To elucidate the reaction mechanisms, a conventional method for kinetic analysis was applied to the master curves. Both surface contracting reactions of spherical and cylindrical sample are fitted for the decomposition of the precursors from the coprecipitates, so that the reaction proceeds from the surface to the inside and the rate is proportional to the reaction surface area. The reasons for these two fitted mechanisms are supposed to be that the shape of the powder sample is not ideal sphere but close to ellipsoid, and that the reaction may proceed to preferential directions of the crystallites. On the other hand, for the film sample of the precursor from the 2-ethylhexanoates solution, diffusion-controlled reaction of plate is the best-fitted mechanism.

(5) Based on the above results, it can be concluded from the kinetic viewpoint that metallic components, i. e., barium, yttrium, and copper are homogeneously distributed in the precursors from the coprecipitates and the mixture of 2-ethylhexanoates, because of the single elementary reaction. The singularity of the elementary reaction can be used as a criterion of the homogeneity in characterization of the precursors.

As seen in the above conclusion, kinetic analysis of thermoanalytical results is versatile, and various informations can be deduced from its conclusion. However, the method described above cannot be applied to the new oxide superconductors, such as the Bi-superconductors, in its original framework because we cannot observe the reaction up to its completion by thermal analysis at usual heating rates due to their low melting temperatures. It is also pointed out that Bi- and Tl-superconductors are formed by disproportionation of a primary product; take Bi-superconductors for instance, $Bi_2Sr_2CaCu_2O_x$ is first formed and then its disproportionation takes place, producing $Bi_2Sr_2Ca_2Cu_3O_x$ and $Bi_2Sr_2CuO_x$ as shown by electron microscopy [37]. Some modification in thermal analysis applications is necessary for these cases.

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