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APPLICATION OF THERMAL ANALYSIS TO KINETIC STUDY OF SUPERCONDUCTING OXIDE FORMATION

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ABSTRACT

Study of superconducting $YBa_2Cu_3O_7$ oxide formation by TG, DTA, EGA and X-ray diffraction is described. Especially, final stage of forming reaction with evolution of CO_2 from $BaCO_3$ is investigated by changing starting materials, such as coprecipitated carbonate, coprecipitated oxalate, homogeneous solution of 2-ethylhexanoates and powder mixture of Y_2O_3, CuO and $BaCO_3$. Phase boundary contracting reaction proceeds for precursors from the coprecipitates, and diffusion controlled reaction for the precorsur from the solution, while multiple parallel processes proceed for the powder mixture.

INTRODUCTION

Thermal analysis is very versatile in ceramic oxide superconductor research, and its usefulness has been shown in numerous papers published since the discovery of high-temperature oxide superconductor. For instance, non-stoichiometry was found by TG,1, 2, 3)and temperature-programmed reduction by TG was applied to estimate the oxygen content.3) The phase diagram was investigated by DTA for crystal growth.4) Thermodilatometry was applied to phase change,3) and it is also useful to thin film formation by investigating the difference in thermal expansion between the film and the substrate.5) Melting accompanied by decomposition6) and glass formation7) were also studied by DTA. Other potential applications are described elsewhere. 8)

Superconducting oxide formation is one of the fields, and TG, DTA and EGA have been applied as well as high-temperature X-ray diffraction. For example, starting materials for sol-gel preparation were examined by TG-DTA9) to detect volatilization.

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The kinetic study of formation is also one of the illustrative applications of thermal analysis, and the results for $YBa_2Cu_3O_7$ by the author and his former coworkers in Electrotechnical Laboratory[1, 10, 11, 12] are summarized in this short review.

RESULTS AND DISCUSSION

Four materials investigated are coprecipitated carbonate, coprecipitated oxalate, homogeneous solution of 2-ethylhexanoates and powder mixture of Y_2O_3, CuO and $BaCO_3$.

A typical result of TG-DTA is shown in Fig. 1.[1] The most interesting stage of weight loss from 800°C to 1000°C was investigated by EGA with a mass-spectrometer, and CO_2 was detected.[10] By comparing TG results of yttrium, copper and barium oxalates published previously, the final stage was assigned to CO_2 evolution from $BaCO_3$.[10] For other materials, similar TG-DTA results were obtained.[11, 12]

Taking account of the above results, the coprecipitated oxalate was heated up to 500°C and cooled. X-ray diffraction was obtained for this precursor by stepwise heating, and the results are reproduced in Fig. 2.[10] The diffraction of the precursor is diffuse and it is not well-crystallized. Sharp diffractions, different from perovskite structure of the superconducting oxide, appeared around 700°C. This result suggests phase separation and crystallization in the precursor. Diffraction around 32°, which is characteristic of the perovskite, appeared above 750°C. The same results were also obtained for the other precursors which were

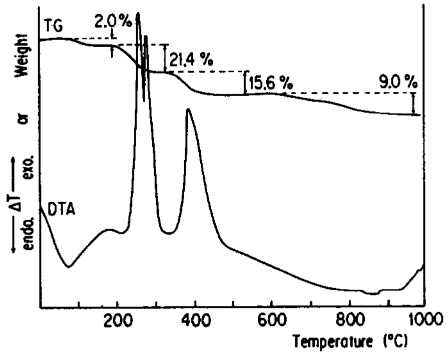


Fig. 1 TG-DTA of coprecipitated oxalate at 15°C/min under oxygen flow

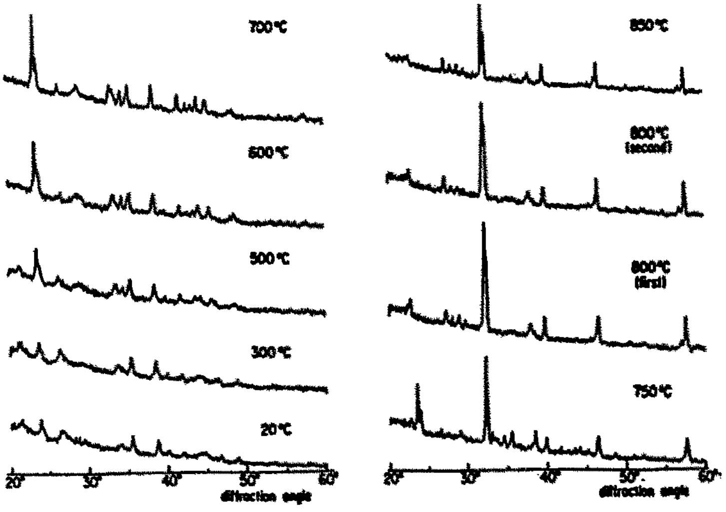
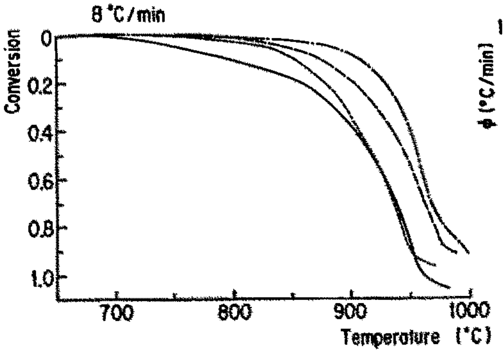


Fig. 2 X-ray diffraction of precursor from oxalate by stepwise heating as indicated.

made by heating the coprecipitated carbonate and dried film prepared from the solution up to 500°C.

Thus, the final stage of formation is decomposition of $BaCO_3$ with CO_2 evolution to form the perovskite, and it is very important to make a homogeneous superconducting oxide of good quality. Therefore, TG of this stage was carried out at different heating rates for the precursors and the powder mixture. Typical results



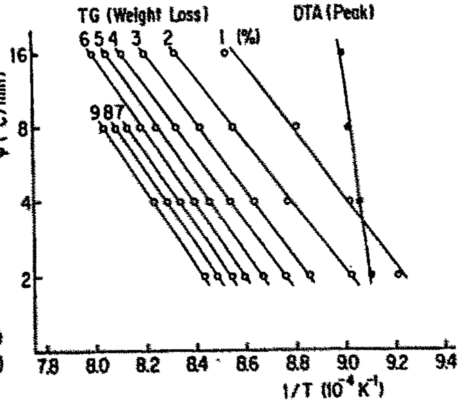


Fig. 3 TG curves of final stage reaction in air.
------- oxalate ·········· carbonate
——— 2ethylhexanoate
—·— powder mixture

Fig. 4 Ozawa plots for oxalate T and ϕ are the absolute temperature and heating rate, respectively.

are reproduced in Fig. 3.[10] To analyze the TG curves the so-called Ozawa plot[13] was applied. One example for the precursor from the oxalate is shown in Fig. 4. As clearly seen, parallel straight lines were obtained and the process is elucidated to consist of a single elementary reaction. In the same temperature range a DTA endothermic peak was observed, and the peak temperature are also plotted in Fig. 4. The slope of the DTA peak temperature is quite different from the other slopes, and the peak is not due to decomposition but presumably due to crystalline transition of $BaCO_3$.

The average activation energy was obtained from the slopes, and it is 263±13 kJ/mol. Similar parallel linear plots were obtained for the precursors from the carbonate and the dried film, and the average activation energies are 282±16 kJ/mol and 269±15 kJ/mol, respectively. On the other hand, plots for the powder mixture were not parallel, as seen in Fig. 5,[12] and this gives evidence of multiple concurrent reactions in this decomposition process. Thus, further analysis of the data for the powder mixture cannot be made by the methods hitherto published.

By using the activation energies estimated above, we can calculate reduced time,[13] and master curves of the weight loss versus the reduced time can be drawn. An example is shown in Fig. 6.[9] Because the reduced time is a hypothetical time for the reaction proceeding at infinite temperature and proportional to the real time, the real times for the isothermal reaction were calculated

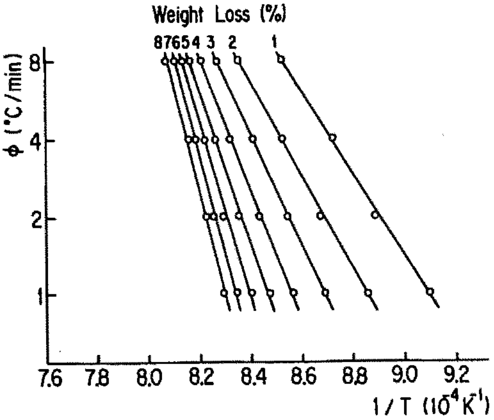


Fig. 5 Ozawa plots for powder mixture

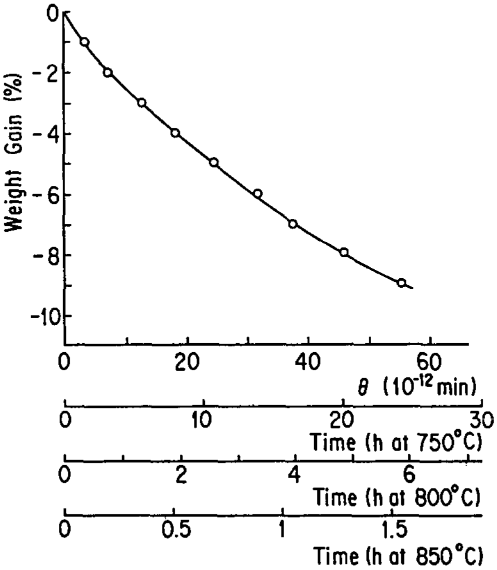


Fig. 6 Master curve for oxalate precursor

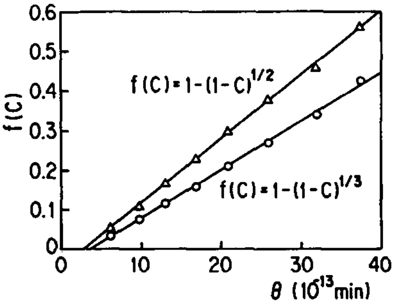


Fig. 7 Analysis of mechanism for carbonate precursor

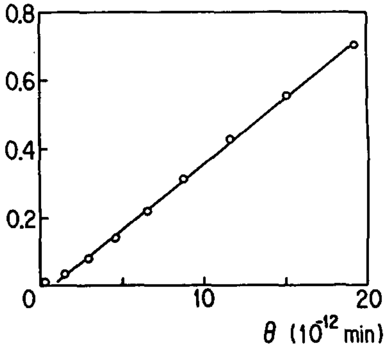


Fig. 8 Analysis of mechanism for 2ethylhexanoate precursor

from the reduced time, as shown in Fig. 6. This is useful for predicting the processes in various temperature modes.

To elucidate the mechanism of the decomposition, the master curves were compared with typical kinetic models. The best fitted model for the precursors from the coprecipitates is phase boundary contracting reaction, but the geometries of the sample, i.e., sphere or cylinder, are equally fitted, as seen in Fig. 7.12) On the other hand, diffusion controlled process of plates is the best fitted model for the precursor from the dried film. The cause for the difference is not clear.

Because the single reaction proceeds in the formation from the precursors, they are homogeneous materials of good quality. Usefulness of thermal analysis is also demonstrated in this investigation.

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