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# NON-STOICHIOMETRY OF $YBa_2Cu_3O_{7-\delta}$ OBSERVED BY REPEATED TEMPERATURE SCANNING

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## Abstract

Repeated temperature scanning method was applied to observe non-stoichiometry of $YBa_2Cu_3O_{7-\delta}$, and interesting results were obtained. Two simultaneously occurring processes were separately observed in mass change; one is a fast process and the other is slow, so that their responses to the temperature change are quite different from each other. The fast process follows the cyclic temperature change, but the slow process is observed to be a gradual mass change. Kinetic behaviors of these two processes are also made clear by plotting the mass *vs*. the temperature. Furthermore, a hysteresis loop was observed in the plot of the mass *vs*. the temperature in a high temperature range presumably due to the third process, and it depends on the heating and cooling rates.

**Keywords:** kinetic, non-stoichiometric compound, repeated temperature scanning method

## Introduction

Non-stoichiometry of some inorganic substances has been one of interesting topics in chemistry [1]. For high temperature oxide superconductors, such as $YBa_2Cu_3O_{7-\delta}$ [2–6], it is very important from both viewpoints of science and technology, because it is closely related with the critical temperature of superconductivity and oxygen vacancies have negative effect on the superconductivity [5, 6]. Therefore, suitable annealing of these materials in oxygen-containing atmosphere is a key to obtain high-performance materials [5]. However, kinetics to approach to equilibrium is very complicated [5], and observation of this non-stoichiometry by repeated temperature scanning would provide us with a new tool for investigating the materials.

On the other hand, a new thermal analysis method by repeated temperature scanning was proposed [7–9], and in this method the sample is repeatedly heated and cooled at constant rates. Observation of non-stoichiometry would be very interesting from a viewpoint of applicability of this new thermoanalytical method, because the mass in equilibrium repeatedly changes by cyclic temperature change and we can observe repeatedly the mass change together with kinetic effect of equilibration. Therefore, it can be expected that the feature of repeated temperature scanning method would be unveiled by this observation.

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When the mass of $YBa_2Cu_3O_{7-\delta}$ was observed by repeated temperature scanning, some additional interesting behaviors were revealed in relation with the above, for instance two processes were separately observed, and the difference is very clear; one is observed as a cyclic change of mass and the other is seen in a long-term gradual mass change. In the cyclic behaviors an additional hysteresis was also seen by kinetic nature of the equilibration, and it seems to be the third process. These results are reported in this short paper.

## Experimental

The powder sample of $YBa_2Cu_3O_{7-\delta}$ was kindly supplied by Hideo Ihara of Agency of Industrial Science and Technology, MITI, Japan, and before the experiments the whole sample was heated at 950°C for 8 h to recover degraded fraction to $YBa_2Cu_3O_{7-\delta}$. The successive runs were made without any sample treatment, so that the thermal history of sample in each run is different from each other. In other word, $\delta$ in the chemical formula was not controlled, so that the relative change in the mass has physical meaning.

The mass change was measured with a thermogravimetry (TG) – differential thermal analysis (DTA) simultaneous apparatus manufactured by Rigaku Corp. (Thermo-plus TG 8210). This apparatus is very suitable for repeated temperature scanning, because infrared lumps are used for heating and its response to the temperature control is very high. The measurements were made under flow of air at 200 mL $min^{-1}$.

## Results and discussion

A typical result is reproduced in Fig. 1. In this measurement, the sample temperature was scanned between 550 and 750°C first at heating and cooling rates of 10 and then at 5°C $min^{-1}$. As seen in this figure, the mass change, i.e., the change of $\delta$ in the chemical formula of sample, consists of two processes. One is a fast cyclic mass change and it quickly follows the temperature change. The other is a gradual mass change and it is just like a changing bias superimposed upon the cyclic mass change. It was reported before [4] that there are two sites of non-stoichiometry; *a* site and *b* site. By appropriate temperature control oxygen content at the *a* site can be zero, while that at *b* site can not be controlled so strictly. Therefore, two processes occur due to these two sites and these seem to correspond to the slow gradual change and the fast cyclic change. The gradual change is caused by difference between the equilibrium outside the scanned temperature range in the previous thermal history and the equilibrium at the present changing temperature, so that it depends on the previous thermal history of the sample. If we observe this phenomenon for long enough time at an appropriate heating and cooling rates, the gradual change would eventually disappear, because the oxygen content at this site would reach to the equilibrium and it could hardly follow the temperature change, while the other cyclic mass oscillation would be maintained, because the oxygen content change due to the other site would quickly follow the equilibrium change. Thus we can recognize separately these two processes easily by repeated temperature scanning.

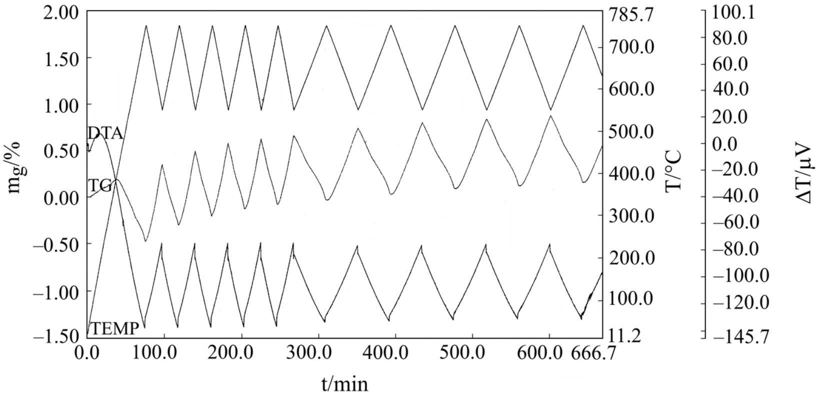

**Fig. 1** A typical TG-DTA curve by repeated temperature scanning between 550 and 750°C under air flow of 200 mL $min^{-1}$; the top curve is temperature, $T$, the middle is mass gain, $m_g$, and the bottom is DTA (temperature difference, $\Delta T$ ), respectively. The run was first done at 10 and then at 5°C $min^{-1}$

When we plot the above result in another way, where the mass is plotted *vs*. the temperature (Lissajous-like plot), we have a different interesting display of the results, as is shown in Fig. 2. In this figure, the mass gain of less than 0.05% in the low temperature range below about 400°C is the apparent mass change due to the change in buoyancy, and from this apparent change we can roughly estimate the similar apparent mass gain in the higher temperature range. Above 400°C the mass changes by the non-stoichiometry. In this figure, the shift of the curve to the upper side corresponds to the gradual change. The cyclic change is expressed as a zigzag line, and these quasi-linear lines are consequence of the quasi-linear temperature dependence of equilibrium oxygen content at the one site in this temperature range. In the cyclic change we can see an interesting behavior, i.e., a hysteresis seen at the high tempera-

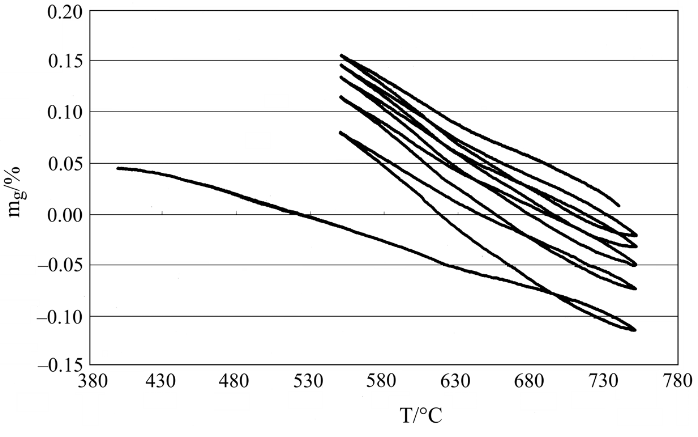

**Fig. 2** A curve of mass gain *vs.* temperature obtained for temperature range between 550 and 750°C at 10°C $min^{-1}$ and later at 5°C $min^{-1}$ under air flow of 200 mL $min^{-1}$

ture turning points, while it is not observed at the low temperature turning points. If we observe the mass at low enough heating and cooling rates, the hysteresis would not be observed, because the mass can follow the equilibrium change. On the other hand, it could not be observed at high enough rates, because the oxygen content at this site cannot follow the equilibrium, as in the above gradual change. Thus, the hysteresis at the high temperature turning points seems to be the third process of the non-stoichiometry.

The hysteresis was considered by a rough theoretical model. In the model, the non-stoichiometry is caused by one site, and the driving force of the cyclic change is assumed to be the difference between the equilibrium mass at the temperature and the actual mass. The rate is assumed to be proportional to this difference. For the sake of simplicity, the cyclic temperature change is assumed to be a sinusoidal oscillation, and also for the sake of simplicity, the rate constant is assumed to be a constant, ignoring the temperature dependence of the rate. The equilibrium mass is also assumed to be linearly dependent on the temperature, as in the case of $YBa_2Cu_3O_{7-\delta}$ in the above temperature range. Thus we have the following equations;

$$\mathrm{d}m/\mathrm{d}t = k(m-m_\mathrm{e}) \tag{1}$$

$$m_\mathrm{e} = m_0-\alpha(T-T_0) \tag{2}$$

$$T = \mathrm{Re}[T_0+A\exp(-j\omega t)] \tag{3}$$

where $m$, $t$, $k$, $T$, $T_0$, $m_\mathrm{e}$ , $m_0$, $\alpha$, $A$, $\omega$ and $j$ are, respectively, the actual mass, the time, the rate constant, the temperature, the constant temperature, the equilibrium mass, the equilibrium mass at $T=T_0$, the constant expressing the temperature dependence of the equilibrium mass, the amplitude of sinusoidal temperature oscillation, its frequency and the unity of imaginary number, and Re[ ] means that the real part in the bracket has physical meaning and that the imaginary part does not.

In the steady state established after long enough time, the long-term gradual mass change disappears, but the mass oscillation occurs and its phase angle is shifted from the temperature oscillation, so that the next equation for the mass oscillation can be assumed:

$$m = \mathrm{Re}[m_0+A^*\exp(-j\omega t)] \tag{4}$$

where $A^*$ is the complex amplitude for the mass oscillation; the complex is used to express the potential phase shift. For these quantities relating with the complex, the following equations hold.

$$A^* = A_\mathrm{r}+jA_\mathrm{i} \tag{5}$$

$$\exp(-j\omega t) = \cos\omega t-j\sin\omega t \tag{6}$$

Introducing Eqs (3) and (4) into Eq. (1) together with the derivative function of Eq. (2), we have the following equation for $A^*$;

$$A^*= \alpha A/(1+\omega^2\tau^2)-j\omega\tau\alpha A/(1+\omega^2\tau^2)$$

where τ equals to $1/k$ and equals to the time necessary for the unconverted fraction to decrease to $1/e$ of the initial quantity. The first term in the right side is the real part and expresses the amplitude of the in-phase oscillation, while the second term is the imaginary part and expresses that of the out-of-phase oscillation. This is just the same as the Debye type dispersion of dielectrics by orientation polarization [10].

When we plot the mass *vs*. the temperature, we have a linear line in the frequency range where $\omega<<k$, because the observed mass follows the equilibrium and the equilibrium mass changes linearly with the temperature. In the range where ω is comparable with $k$, we have ellipsoidal curve such as in a Lissajous figure, and the mass change cycle is not in the same phase with the temperature cycle. The maximum out-of-phase change occurs at $\omega=k$. In the range where $\omega>>k$, the mass change does not occur and it does not follow the cyclic temperature change.

The above theoretical considerations are based on a roughly approximated model, and the rate constant $k$ seems not a constant but dependent on the temperature, while the temperature is changed in the above experiments not in sinusoidal way but at a constant rate. However, the behavior in the cyclic temperature change in the above experiments seems essentially the same as predicted by the theoretical considerations.

Therefore, the dependence of the hysteresis on the heating and cooling rate (or the frequency dependence) is investigated in a relatively narrow temperature range. Because the crystalline structural change occurs at about 650°C between orthorhombic and tetragonal phases [5, 6] the observation was made in a temperature range between 550 and 650°C and also in another temperature range from 650 to 750°C. A typical results obtained by the scanning between 550 and 650°C is shown in Fig. 3, and the data are plotted in the Lissajous-like way, because the behavior can be observed more clearly than in usual TG curves. The results are shown in Fig. 4 together with the other data obtained at different rates. In all Lissajous figures quasi-linear lines are observed and the mass changes in equilibrium, except the gradual mass change.

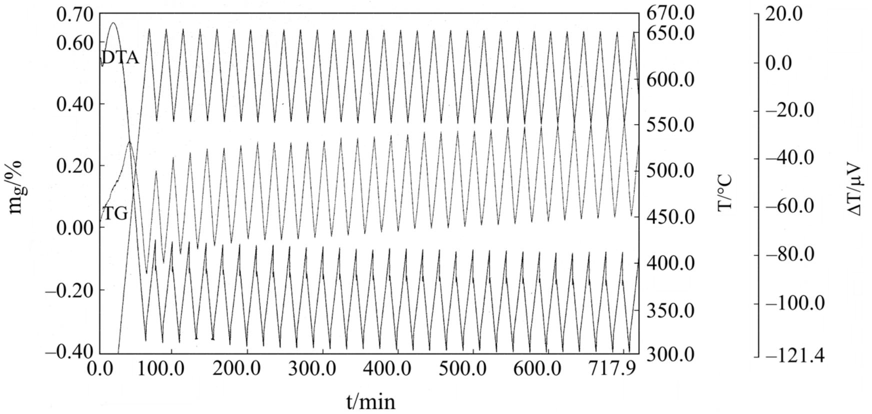

**Fig. 3** A typical TG-DTA curve by repeated temperature scanning between 550 and 650°C at 10°C $min^{-1}$ under air flow of 200 mL $min^{-1}$; the top curve is temperature, the middle is mass gain and the bottom is DTA (temperature difference), respectively

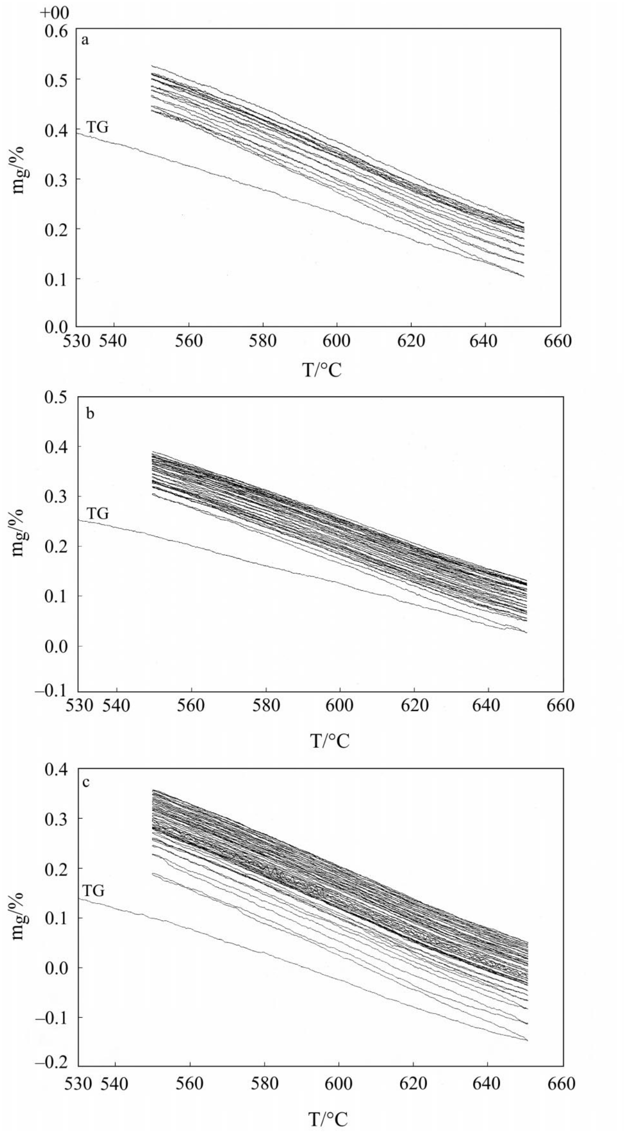

**Fig. 4a–c** Curves of mass gain *vs*. temperature obtained for temperature range between 550 and 650°C by heating and cooling rates of a – 2°C $min^{-1}$; b – 5°C $min^{-1}$; c – 10°C $min^{-1}$, respectively

On the other hand, the behavior in a temperature range between 650 and 750°C is somewhat different. One of the typical results is shown similarly in Fig. 5, and the Lissajous figures are reproduced in Fig. 6. As is seen in Fig. 5, the triangular mass change is somewhat distorted. The hysteresis and its dependence on the heating and cooling rates are more clearly seen in Lissajous figures (Fig. 6); deviation from the equilibrium mass change is clearly observed in the hysteresis at the high temperature turning points. The

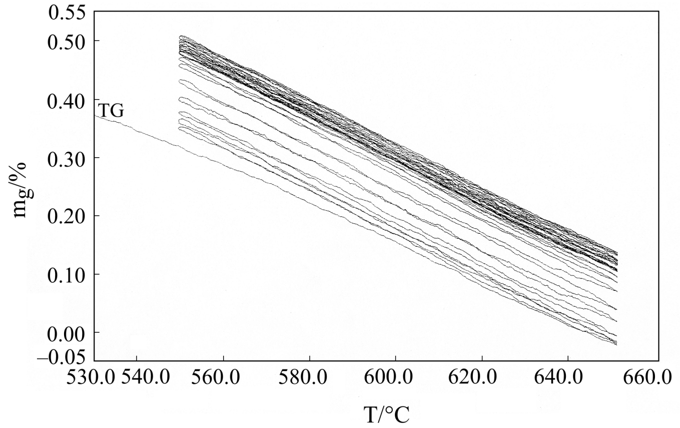

**Fig. 4d** Curves of mass gain *vs*. temperature obtained for temperature range between 550 and 650°C by heating and cooling rates of 20°C $min^{-1}$, respectively

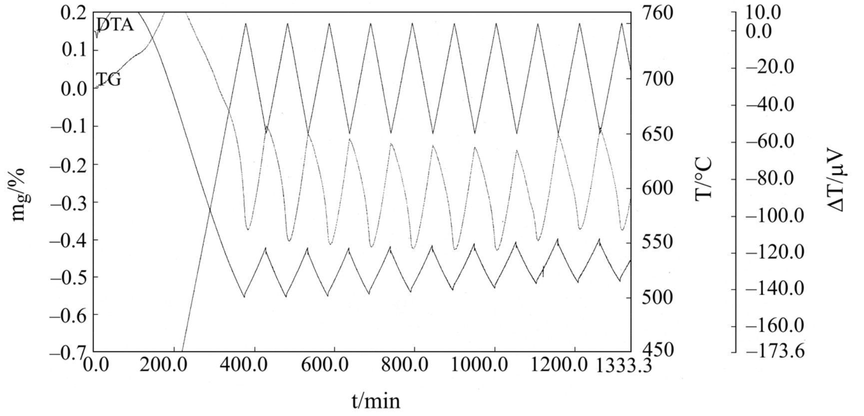

**Fig. 5** A typical TG-DTA curve by repeated temperature scanning between 650 and 750°C at 2°C $min^{-1}$ under air flow of 200 mL $min^{-1}$; the top curve is temperature, the middle is mass gain and the bottom is DTA (temperature difference), respectively

deviation is the largest for the heating and cooling rate of 2°C $min^{-1}$, and the deviation decreases with increase in the rates. Thus the rate of the equilibration seems to become comparable with the heating and cooling rates less than 2°C $min^{-1}$ (or at the frequency of roughly 1/6000 $s^{-1}$) in this temperature range, and the rate constant can be roughly estimated from this value of frequency. It can be concluded that this hysteresis is caused by the third process, and it can be more clearly observed in the high temperature turning point, because the equilibration becomes detectable first in the high temperature range. On the other hand, the behavior is the same as that in Fig. 4 at the high rates and at the low temperature turning points, because the third process does not proceed in these temperature and/or frequency ranges.

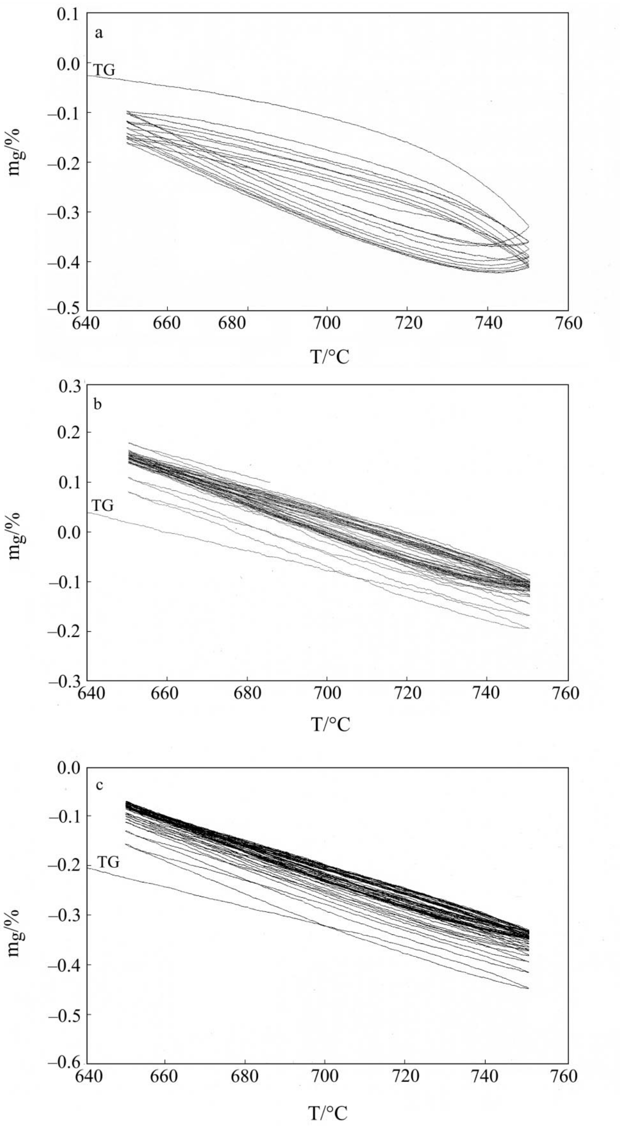

**Fig. 6a–c** Curves of mass gain *vs*. temperature obtained for temperature range between 650 and 750°C by heating and cooling rates of a – 2°C $min^{-1}$; b – 5°C $min^{-1}$; c – 10°C $min^{-1}$, respectively

By the repeated temperature scanning, the equilibrium and the equilibration are separately observed, and the display in Lissajous figures clearly reveals the kinetic nature of the non-stoichiometry. Thus, its potential applicability is clearly shown in this paper. It would be also useful in characterization of superconducting materials and in other cases of equilibrium and equilibration. Similarly the equilibrium and the equilibration would be

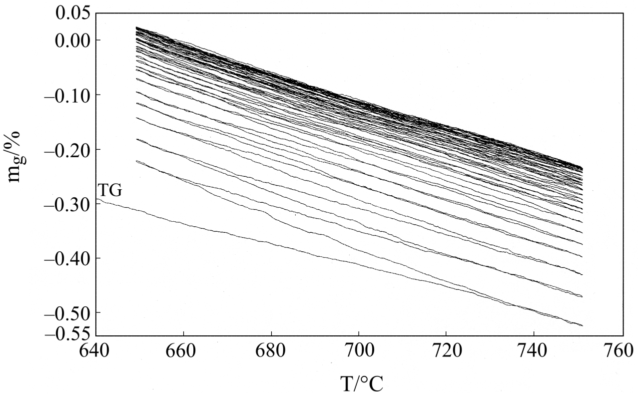

**Fig. 6d** Curves of mass gain *vs*. temperature obtained for temperature range between 650 and 750°C by heating and cooling rates of 20°C $min^{-1}$, respectively

observed by sinusoidal temperature modulation [11] respectively as the amplitude and the imaginary part, though the process is non-linear in its essence.

For other chemical processes, this method would be useful to elucidate similar behavior, which cannot be clearly unveiled by the conventional temperature control, but by observing a certain physical property of the sample either in the repeated temperature scanning or in sinusoidal temperature modulation. One of possible applications would be steady state and approach to the steady state [9].

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