Journal of Thermal Analysis and Calorimetry, Vol. 55 (1999) 691-698

THERMAL DECOMPOSITIONS OF (RE)$Ba_2Cu_3O_6$ (*RE*=Y, Nd, Er)

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Abstract

Thermogravimetric *in situ* measurements of oxygen loss from (RE)$Ba_2Cu_3O_6$ samples (*RE*=Y, Nd, Er) heated isothermally in a relatively high dynamic vacuum were made with a Cahn RG electrobalance. Single-phase orthorhombic samples of composition (RE)$Ba_2Cu_3O_{7-x}$ (highest oxygen content) were synthesized from stoichiometric (1:2:3) mixtures of high-purity $(RE)_2O_3$, $BaCO_3$ and CuO. The original 1:2:3 mixture was prepared by the two-stage procedure described earlier. The crystal structure of the sample in the original orthorhombic phase was controlled by the X-ray powder method (CuK_α radiation) using a Stadi P Stoe diffractometer with a position-sensitive detector. The decomposition curves are described by the sum of exponential terms corresponding to rapid and slow first-order processes in which differently sized grains of the powder samples are involved. The activation energies are estimated from appropriate Arrhenius plots.

Keywords: activation energy, kinetics, solid-state reactions, superconductors, thermogravimetry

Introduction

Numerous studies have revealed that the properties of (RE)$Ba_2Cu_3O_{7-x}$ (*RE*=rare earth) superconductors are strongly dependent upon the oxygen content and oxygen ordering. It is therefore important to study and understand the behaviour of the oxygen ions and associated point defects in these compounds.

Powder neutron diffraction [1–4] and X-ray absorption fine structure (XAFS) experiments [5] have demonstrated that decrease of the oxygen content results in a progressive depopulation of oxygen from the O(1) chain sites, with no detectable change in the occupancy of the O(2) and O(3) sites in the Cu(2)–O plane. For samples quenched from high temperature there is also evidence for additional vacancies at the bridging O(4) oxygen site between Cu(1) and Cu(2) [3, 4, 6, 7]. However, it is not certain whether the O(4) vacancies are associated with alternate Cu(1)–O chains or are randomly distributed.

Oxygen ordering is temperature-dependent and T_c of (RE)$Ba_2Cu_3O_{7-x}$ can therefore be changed at constant oxygen content by storing the samples at temperature $0°C<T_c<150°C$.

1418–2874/99/ \$ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

The energetics of removable oxygen binding in the '123' compounds has mostly been examined in yttrium preparations [8–21]. The values of the relevant activation energies obtained from various measurements (thermogravimetry, calorimetry, resistivity, etc.) lie between 0.9 and 1.7 eV. This may be attributed in part to differences in experimental conditions. An additional complication is the fact that $(RE)Ba_2Cu_3O_{7-x}$ is a mixed conductor in which charge may be transported by both electronic and ionic carriers. The extremely high oxygen diffusion coefficients in these compounds allow oxidation, reduction and also oxygen isotope exchange at very low temperatures [22, 23].

This paper presents the results of thermogravimetric *in situ* measurements of oxygen loss from $(RE)Ba_2Cu_3O_6$ (RE=Y, Nd, Er) in dynamic vacuum with a Cahn RG electrobalance.

The studies allow establishment of the thermodynamic and kinetic conditions for the decomposition. Investigations of the thermal decomposition of $(RE)Ba_2Cu_3O_6$ in dynamic vacuum are valuable, particularly in view of the high oxygen diffusion coefficient in these cuprates. Dynamic vacuum protects against the readsorption of oxygen from the environment. This paper reports on the influence of the ionic radius of RE on the bonding of the oxygen atoms in the Cu(2)–O planes.

Experimental

Single-phase orthorhombic samples of composition $(RE)Ba_2Cu_3O_{7-x}$ (highest oxygen content) were synthesized from stoichiometric (1:2:3) mixtures of high-purity $(RE)_2O_3$, $BaCO_3$ and CuO. The original 1:2:3 mixture was prepared in a two-stage procedure. Firstly, $BaCO_3$ and CuO in a molar ratio of 2:3 were thoroughly mixed and ground in an agate mortar. Next, the appropriate quantity of $(RE)_2O_3$ was added and the whole was mixed and ground again. This mixture, in the form of loose powder in an alumina boat, was heated at 950°C in flowing oxygen during 4 h. After slow cooling to room temperature, the sample was reground and heated under the same conditions during a further 4 h. Subsequently, the temperature was lowered to about 400°C, and the sample was kept at this temperature during 15 h (still in oxygen) and then slowly cooled to room temperature. X-ray examinations revealed that the synthesis was virtually complete after the first heating. The *in situ* measurements of the oxygen loss were performed in a Cahn RG ultramicrobalance system permitting the decomposition to be followed in a dynamic vacuum of $\approx 10^{-6}$ torr. The samples were heated up to the temperature of the experiment at a constant rate of 10°C min^{-1}. The initial mass of the samples was ca 80 mg and the fall in mass caused by the loss of one oxygen atom per chemical formula $[(RE)Ba_2Cu_3O_7 \rightarrow (RE)Ba_2Cu_3O_6+1/2O_2\uparrow]$ corresponded to ≈2 mg. In order to determine disturbances which affect the accuracy of weighing in vacuum or in a controlled atmosphere [24–26], blank runs were used to correct the data obtained during kinetic runs.

The apparent mass changes did not exceed ±20 μg. As the accuracy of the measurements was better than ±20 μg, our estimate of the content in the sample was at the level of at least ±0.01 atom per chemical formula. Loose-powder (RE)$Ba_2Cu_3O_7$ samples were placed in a small quartz crucible in the vicinity of a NiCr-Ni thermocouple. The system was first evacuated down to 10^{-4} Pa and the sample was annealed at 120°C during 20 h to remove adsorbed gases and moisture. It was then heated up to the temperature of the measurement at a constant rate of 10°C min^{-1}.

To ensure a constant grain size distribution, the small samples used in the measurements were always taken from a larger portion of an original (RE)$Ba_2Cu_3O_7$ preparation. In most instances, the measurement duration was long enough (sometimes up to 200 h) for equilibirium to be approached. The crystal structures of the samples in the original orthorhombic phase were controlled by the X-ray powder method (CuK_α radiation), using a Stadi P Stoe diffractometer with a position-sensitive detector.

Results and discussion

The oxygen loss measurements were performed on different (RE)$Ba_2Cu_3O_6$ (*RE*=Y, Er, Nd) preparations (in the initial state x_t=0) isothermally heated in the range 700–850°C. Decomposition of the samples started after the isothermal temperature was reached. Oxygen loss curves are exemplified in Fig. 1 for $YBa_2Cu_3O_6$. Prior to furher analysis, the oxygen loss data (x_t values) were normalized. In this case, desorbing oxygen is associated with total decomposition of

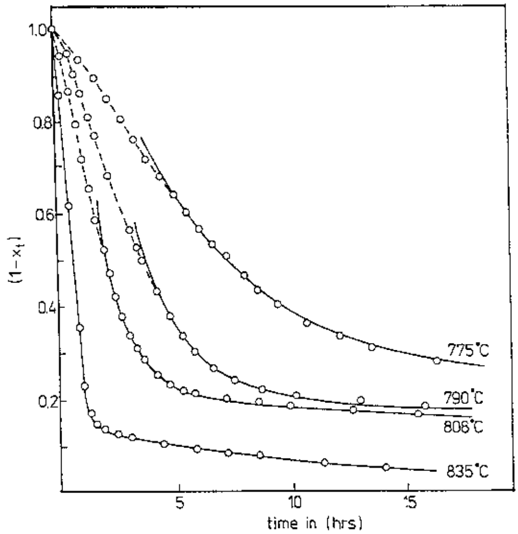

Fig. 1 Plot of $(1-x_t)$ *vs.* time for yttrium preparation

the tetragonal structure of compounds into non-identified products, where the copper is monovalent in the final stage. The final oxygen content in the formula should always be equal to 5, independently of the thermal decomposition.

Decomposition of the type

$$(RE)Ba_2Cu_3O_6 \rightarrow \text{‘}(RE)Ba_2Cu_3O_5\text{’} + 1/2O_2\uparrow$$

$$\text{‘}(RE)Ba_2Cu_3O_5\text{’} = 1/2(RE_2O_3)\cdot 2BaO\cdot 3/2Cu_2O$$

at constant temperature should follow a simple exponential relation (a first-order process) if all grains of the preparation are of the same size. The bonding of the oxygen atoms was investigated by means of gas evolution measurments and interpreted in terms of a first-order desorption model for the evolution process [19]. As our samples consisted of grains of different sizes, which decomposed at different rates, we anticipated that the overall oxygen loss may be described by the sum of an appropriate number of exponential terms, depending on the grain size distribution. It has been found that for our powdered samples the number of such exponents can be limited to two terms, corresponding to high and low decomposition rates, in which small and large grains are involved:

$$(1 - x_t) = Ae^{-k_1 t} + Be^{-k_2 t} \tag{1}$$

where x_t is the value reached after time t, while k_1 and k_2 are the rate constants. The solid lines in Fig. 1 were calculated by using the above equation and appropriate constants. It should be emphasized that the agreement between the calculated and experimental results is quite good.

Utilizing the Arrhenius relationship, we plotted log$k$ (k_1 or k_2) *vs.* reciprocal temperature (Fig. 2). The activation energies estimated for $(RE)Ba_2Cu_3O_6$

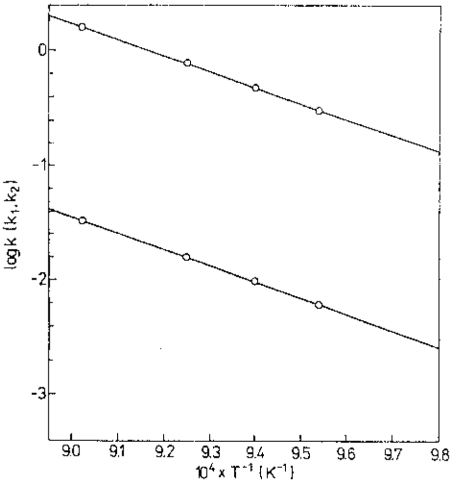

Fig. 2 Arrhenius plots for yttrium preparation

(*RE*=Er, Y, Nd) were 3.2, 3.0 and 2.7 eV, respectively. The activation energy of oxygen loss is a reciprocal function of the ionic radius of $(RE)^{3+}$ [19, 27] in these cuprates.

Studies of the oxygen content and ordering in the different '123' phases show that, as the RE ion size increases, the rate of fall in T_c with oxygen content increases [28–30] and the plateau width becomes narrower, as shown in Fig. 3. The critical temperatures T_c of the samples were determined by the standard four-probe resistivity method.

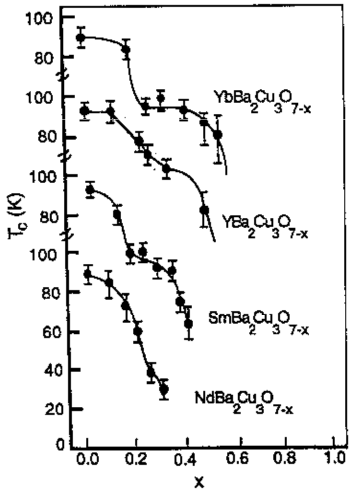

Fig. 3 T_c *vs*. oxygen deficiency x in $(RE)Ba_2Cu_3O_{7-x}$ with increasing RE ionic radius from Yb to Y to Sm to Nd, adapted from Krekels *et al.* [29]

In air, the orthorhombic to tetragonal phase transition temperature decreases rapidly with increasing RE size from ≈750°C for Er to ≈550°C for Nd [31]. The implications are that tetragonal REBCO exists over a much wider temperature region for large REs. For example, in air, tetragonal YBCO exists over the temperature range ≈1003–650°C=353°C, whereas the corresponding polymorph of NdBCO exists over the temperature range 1142–550°C=592°C. In effect, the REBCOs of larger REs have higher entropy and the oxygen is more disordered than for the smaller REs. Consequently, the low-temperature ordered superstructures are predicted to form at lower temperatures and higher oxygen contents for the larger REs. Experimental evidence for this comes from thermodynamic studies on NdBaCuO [32].

The existence of two plateaux, at 90 K and 60 K, in the T_c *vs*. oxygen stoichiometry plots is related to the existence of the different oxygen superstructure regions. A phase separation model has been put forward to explain the effect [33–40]. Evidence for phase separation near 7–x=7.0 has been demonstrated by Claus *et al.* [38] in structural and electrical characterization studies on single crystals. The same crystal was found to have two distinct *c* parameters, and the resistivity and magnetic susceptibility were found to be broadened at T_c. In another study on single crystals, the *c* parameter was found to increase beyond optimal doping, and a distinct double transition was observed in the susceptibility data [40].

The use of doping to modify the defect structure and properties in REBCO is growing in importance in relation to both device manufacture (e.g. for barrier layers and contacts) and bulk processing (e.g. for seeding and joining). For doping at all the possible cation sites in REBCO, there is known to be a strong influence on the oxygen content, ordering and mobility. Future progress in applications of doped REBCO materials will stand to gain from detailed studies of the influence of the chemistry on the oxygen thermodynamics and kinetics.

Conclusions

The results obtained indicate that the phase separation in REBCO '123' compounds is connected with heterogeneous distribution of the charges in the Cu(2)–O planes. For systematic progress, basic research into the thermodynamics and materials chemistry should proceed in parallel with processing studies.

More experiments on well-characterized samples are required, and quantum chemistry calculations are extremely necessary, because the role of geometric and electronic factors in these compounds is still unclear. Such calculations can be fundamental as concerns the theory and mechanism of high-T_c superconductivity.

Further basic knowledge of the high-temperature chemistry of REBCO for a wide range of rare earths, and with apropriate dopant additions is necessary for the successful application of these materials in bulk and thin film form.

The superconducting quantum interference device (or SQUID) is used to detect extremely weak magnetic signals by electrical activities in the brain and heart. For these applications, it is crucial to bring the detector as close as possible to the source of the field, a task that will be easier to accomplish with a high-T_c SQUID cooled by liquid nitrogen than with the conventional liquid helium-cooled device. Liquid nitrogen is about 10 times cheaper than liquid helium, but, more importantly, liquid nitrogen is a more effective coolant because of its larger heat of vaporization. Probably the first necessary, indeed essential, application will be wires made from these cuprate superconductors.

Y-123 has been the material of choice for such applications because it retains high critical currents in epitaxial films or single crystals. In 1995, research at the Los Alamos National Laboratory led to a record current-carrying capacity at 77 K.

The Y-123 films were capable of carrying more than 100 A, with a critical current capacity of over 10^6 A cm^{-2}, well above the requirements for electrical transmission lines.

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