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Thermal analysis of iodine deintercalation of the compound I-$Bi_2Sr_2CaCu_2O_{8+x}$

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Abstract

Deintercalation of iodine from the compound I-$Bi_2Sr_2CaCu_2O_{8+x}$ was investigated by thermogravimetry (TG) and X-ray diffraction carried out at the different stages of the process.

A conventional non-isothermal kinetic analysis and a constant rate thermal analysis of the iodine deintercalation process were performed: as a result, a two step model of the iodine release is proposed.

Keywords: Bismuth cuprate; Intercalation

1. Introduction

The crystal structures of the $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$ (n = 1–3)-type superconductors consist of perovskite blocks separated by weakly bound Bi-O layers between which it was shown that intercalation of chemical species was possible [1–8]. The intercalation changes the distance between perovskite blocks and hence between the Cu–O planes which are believed to be responsible for superconductivity in this system; a modification of the anisotropy of the properties of these superconductors is therefore expected.

Examination of the different intercalation studies of these compounds shows that the most extensively studied intercalant is iodine for which the most reliable data were obtained. Iodine intercalation between the Bi-O layers leads to important changes such as:

- the distance between the perovskite blocks increases by a distance of 7Å per cell [1],
- the perovskite stacking sequence changes from A-B-A to A-A-A upon intercalation, leading to space-group changes of the lattice,
- the normal state electrical properties are modified: the intercalated compound is a metallic-type conductor along the c axis (i.e. perpendicular to the Bi-O layers) whereas the pristine compound has semiconducting behaviour [9].

In spite of these important structural changes the superconducting properties are not much changed by the iodine intercalation. There is also evidence for a hole doping process due to the intercalation

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[10–11]. However, even with the research effort carried out on iodine intercalation in these compounds, in particular in $Bi_2Sr_2CaCu_2O_8$(2212), there are still uncertainities concerning the in-plane iodine distribution [12] (recently, a model was proposed by Stoto et al. [13]).

We though therefore that a careful study of the deintercalation of iodine from the I-2212 compound could provide information regarding the iodine distribution in this compound. We have therefore undertaken thermogravimetric experiments in order to make a conventional non-isothermal analysis of the deintercalation together with a constant rate thermal analysis (CRTA) of the process. X-ray powder diffraction was carried out in parallel at the different stages of the deintercalation.

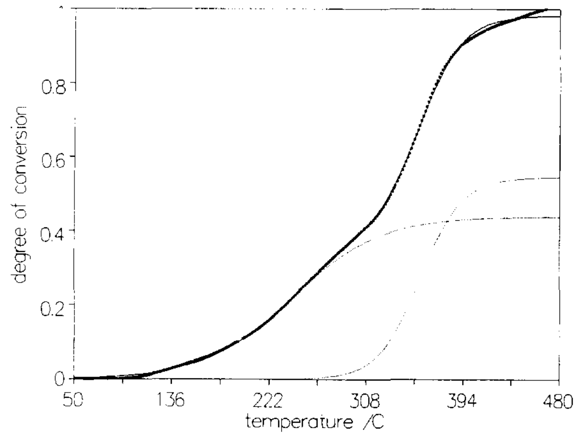

Fig 1. Variation with temperature of the conversion degree α corresponding to the deintercalation reaction (* experimental points, ... suggested decomposition steps).

2. Experimental

The intercalated I-2212 compound was obtained by reacting 2212 powder and iodine in a sealed evacuated pyrex tube (10^{-3} torr) at 190°C for four days. The 2212 powder was prepared according to the procedure described by Maeda et al. [14].

Complete synthesis of 2212-I and 2212 was checked by X-ray powder diffractometry. A Philips PW3710 equipment with nickel filtered Cu Kα radiation was used.The unit cell parameters were refined by a whole pattern Rietveld method [15].

The thermal analysis data were obtained using two derivatographs MOM Budapest of the type Paulik-Paulik-Erdey, namely Q-1500 D and C types. Samples were heated in a static air atmosphere at heating rates ranging from 1.5K/min to 10K/min. In the constant rate thermal analysis the heating rates were adjusted to be in the decomposition dα/dt range 1.5×10^{-4} to 4.5×10^{-4} s^{-1}. To evaluate the non-isothermal kinetic parameters, three integral methods were used, namely that of Coats-Redfern [16] that of Flynn-Wall [17] for the constant heating rate and a modified Coats-Redfern [18] procedure. The kinetic analysis of the CRTA data was performed using the method described by Fatu and Segal [19]. The calculations were performed with computer programs written by the authors [20].

3. Results and discussion

The degree of conversion *vs* time curves obtained in the nonisothermal condition exhibit a shape corresponding to the superposition of two decomposition steps thus suggesting a two-step elimination process (see Fig. 1). We have therefore attempted to separate these steps for a kinetic analysis.

3.1. *X-ray powder diffraction*

The X-ray powder diffractogram of the starting compound submitted to deintercalation corresponds to that of 2212-I [21] with a = b = 5.41Å and c = 18.86Å and a P space group. The X-ray powder diffraction of the product resulting from the total deintercalation reaction is that of the 2212 compound with a = b = 5.41Å and c = 30.69Å with a B space group (for a discussion of the structures of 2212 and 2212-I, as well as those corresponding to the different stages of iodine intercalation in 2212, see reference [22]).

The material corresponding to the first deintercalation step which we recorded at composition 2212-$I_{0.55}$ shows no specific diffraction lines besides those of the 2212 and 2212-I compounds. This is in

Table 1
Interplanar distances (Å), relative intensies and Miller indexes for 2212-I and 2212-I_x

2212-I			$2212-I_x$		
d(Å)	Irel	hkl	d(Å)	Irel	hkl
3.769	50	005	3.846	20	*008*
3.547	15	014	3.547	15	*113*
3.243	70	113	3.260	95	113, *115*
3.131	40	006	3.078	50	006, *0010*
2.897	20	016*	2.949	35	016*
2.698	100	007, 200	2.710	100	007
			2.673	20	200

* Corresponds to an impurity line usually present in the 2212 phase

good agreement with the observation of Koike et al. [23] who mentioned that at various iodine contents of the intercalation process there are no observable X-ray diffraction lines due to higher intercalation stages. Table 1 lists the interplanar distances and the corresponding Miller indices of the reflections of 2212-I and 2212-I_x in a 2Θ range varying from 20 to 35 (i.e. for d values varying from 4.4Å to 2.5Å). The hkl lines marked in italic characters belong to the 2212 cell and this means that the 2212 phase is still present together with the 2212-I_x phase..

As can be seen, the intermediate step does not correspond to a stage-2 intercalation phase but to a mixture of the 2212 and 2212-I phases.

3.2. *Non-isothermal kinetic analysis*

In all our experiments a two-step iodine release with slightly superimposed steps was found. Using a simple mathematical procedure we have separated these two steps as follows.

The mathematical analysis is based on the assumption that the TG curves of the solid-gas decomposition representing the variation of the degree of conversion α with temperature have a sigmoid shape coresponding to the equation:

$$\alpha(T) = a_0/(1 + \exp(-(T - a_1)/a_2)) \tag{1}$$

where a_0, a_1 and a_2 are the amplitude, the position and the width of the sigmoid, respectively. As a consequence, a_0 is the maximum height of the sigmoid and a_1 is the value of the decomposition temperature.

In order to extract the two independent TG curves we have minimised the difference between the recorded degree of conversion and the sum of the two sigmoids. The minimum of the function:

$$\Delta = (Y_{exp} - (\alpha_1(T) - \alpha_2(T)))^2 \tag{2}$$

leads to the sigmoid parameters with the condition that the sum of the amplitudes of these sigmoids should be equal to the overall degree of conversion.

Figure 1 shows the α *vs* T graph: on the figure the experimental points, the two suggested steps and the computed curve are plotted.

Table 2 lists the values of the sigmoid parameters and a statistical indicator χ^2 of the fitting procedure, for the decomposition of 2212-I at various heating rates. As can be seen, the iodine distribution between the two release steps does not depend on the heating rate. The χ^2 values are a convincing indica-

Table 2
Values of the sigmoid parameters obtained in the minimization process for various heating rates. The sigmoid is defined here as: $S(T) = a_0/(1 + \exp(-(T - a_1)/a_2)$.

	1.5K/min	2.5K/min	10K/min
a_0(1st step)	0.453	0.465	0.464
a_1(1st step)	233.0	247.3	246.9
a_2(1st step)	39.4	40.8	45.7
a_0(2nd step)	0.527	0.514	0.526
a_1(2nd step)	346.9	356.4	376.4
a_2(2nd step)	17.4	17.0	23.6
χ^2	0.008542	0.009118	0.006807

Table 3
Values of the non-isothermal kinetic parameters for the deintercalation steps.

	1st step	2nd step
Activation energy (kJ/mol)	39.81 ± 0.09	151.9 ± 0.4
preexp. factor (s^{-1})	14.1 ± 0.0001	$6.7 \times 10^9 \pm 0.0002$
reaction order	1.20	1.60
Correlation coefficient	-0.999949	-0.999963

tion of the accuracy of the results. We see that, in the considered heating rate range the decomposition mechanism as well as the amount of the released iodine in each step do not change.

The two decomposition steps can be described by the following equations:

$$2212\text{-}I \rightarrow 2212\text{-}I_{0.55} + 0.225\ I_2 \qquad (3)$$

$$2212\text{-}I_{0.55} \rightarrow 2212 + 0.275\ I_2 \qquad (4)$$

We have calculated the non-isothermal kinetic parameters of the reactions using the three previously mentioned integral methods in the heating rate range 1.5K/min to 10K/min. Taking into account the agreement between the values of the non-isothermal kinetic parameters which were obtained as well as their independence on the heating rate, we have listed in Table 3 the results obtained with the Flynn-Wall method only, for a rate of 1.5K/min. These non-isothermal parameters were calculated with α values computed with the sigmoid parameters listed in Table 2. Taking into account the values of the correlation coefficient, as well as the χ^2 values, a description of the iodine release can be proposed based on the values of the kinetic parameters. (This calculation method is less likely to generate errors because, in the minimisation process, there are no approximations in the function shape). In another analysis, we have tried to separate the conditions corresponding to the two steps using a minimisation function:

$$\Delta = (Y_{exp} - \alpha'_1(A, E, n) - \alpha'_2(A, E, n))^2 \qquad (5)$$

where $\alpha'_1(A, E, n)$ and $\alpha'_2(A, E, n)$ are the Coats-Redfern expressions for the degree of conversion. There are two drastic approximations in this equation:

- the asymptotic approximation of the temperature integral taking into account only the first two terms in the corresponding series
- the Coats-Redfern assumption that $2/x$, where $x = -E/RT$, is negligible with respect to unity. These approximations are unfavourable and can lead to errors, especially when the activation energy is low [24–25]).

It is important to note the difference between the activation energies of the two iodine release processes. The value corresponding to the first step suggests a *physical* absorption of iodine whereas the activation energy of the second step is more likely that of a *chemical* absorption.

3.3. Constant rate thermal analysis

CRTA is a useful technique to examine a two step TG curve and to determine the conversion function $f(\alpha)$ of the decomposition.

The rate of a decomposition is given by:

$$d\alpha/dt = A\, f(\alpha) \exp(-E_a/RT), \qquad (6)$$

where α is the degree of conversion, t is time, A the pre-exponential factor, E the activation energy, R the gas constant and T the temperature in K; $f(\alpha)$ is the conversion function which depends on the particular reaction mechanism.

In the CRTA approach one takes the general conversion function:

$$f(\alpha) = (1 - \alpha)^n \alpha^m, \qquad (7)$$

with the purpose of obtaining the parameters **n** and **m**.

If we impose a heating program in order to maintain $d\alpha/dt$ at a constant value, the variable t can be eliminated:

$$\alpha = Ct \text{ and,} \tag{8}$$

$$A \exp(-E_a/RT) = C/f(\alpha) \text{ or,} \tag{9}$$

$$\ln A - E/RT + \ln f(\alpha) = \ln C, \text{ and} \tag{10}$$

$$dT/d\alpha = -RT^2/E\,(d \ln f(\alpha))/d\alpha \tag{11}$$

The condition $dT/d\alpha = 0$ for the minimum of the T *vs* α curve, leads to

$$m/n = \alpha'/(1-\alpha'), \tag{12}$$

where α' is the degree of conversion at the temperature of the minimum. An estimation of the parameters m and n is possible in CRTA methods using relations (10) and (11).
There are two limiting cases:

- when $dT/d\alpha > 0$ we have $m = 0$
- when $dT/d\alpha < 0$ we have $n = 0$ (see reference [19] for details).

A typical CRTA curve for the deintercalation of iodine is plotted in Figure 2 (the imposed decomposition rate was $d\alpha/dt = 0.00031\ s^{-1}$). As can be seen, there are two release steps with a slight change of the slope. For the first step it is difficult to stabilize a constant decomposition rate because the process has a low activation energy; hence the decomposition rate does not change much with temperature. Therefore we could not evaluate the CRTA kinetic parameters for this first decomposition step. A better plot showing the difference of the decomposition rates associated with these steps is mass *vs* T (Figure 3). The CRTA curve exhibits a change in slope. It is obvious that there are two decomposition steps with different reaction rates.

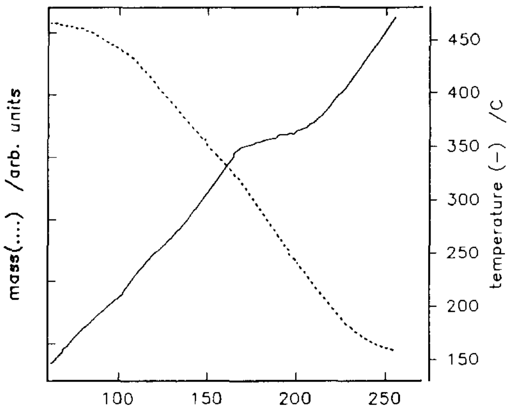

Fig 2. CRTA curve for the decomposition of 2212-I decomposition in a mass vs time and temperature vs time representation.

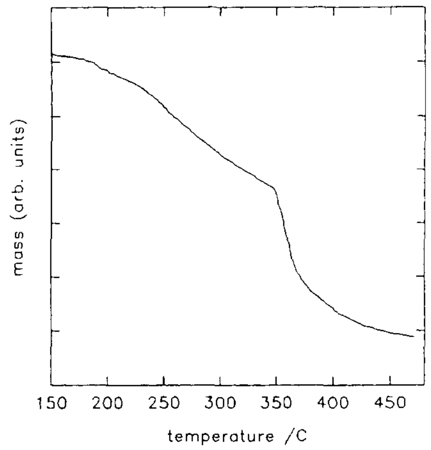

Fig 3. Mass vs temperature curve for a CRTA experiment (the change in slope is due to the change in the decomposition rate).

The T *vs* α'' curve, where α'' is the degree of conversion for the second reaction (the degree of conversion was obtained from the stoichiometry of reactions 3 and 4) is plotted on Figure 4. It can be seen that $dT/d\alpha > 0$; then $m = 0$ and the conversion function is $f(\alpha) = (1-\alpha)^n$ (the same type of curve was obtained for the first deintercalation step). Under these circumstances we can consider that the kinetic parameters obtained in the non-isothermal analysis are correct at least for the form of the conversion function.

For the second decomposition step, the CRTA kinetic parameters which we have obtained are :

$E_a = 107$ kJ/mol

$A = 1.1 \times 10^6\ s^{-1}$

$m = 0$

$n = 1.25$

The difference between these values of the activation parameters and those of Table 3 can be accounted for by a *compensation effect*, i.e., a linear correlation between ln A and E_a[26]; any error in the determination of E_a leads to an equivalent error in the value

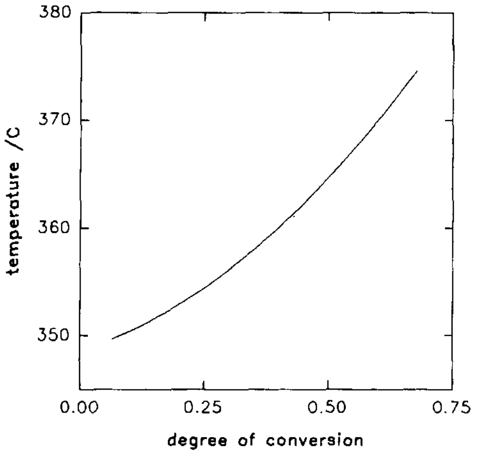

Fig 4. Temperature vs α curve for the second decomposition step obtained with the CRTA method (only the range of α for which the iso-kinetic condition fulfilled was considered).

of ln A. In this example, a lower activation energy is compensated by a lower preexponential factor. If we compute the kinetic constant k with the Arrhenius equation for the two sets of values, we obtain (at 346°C, which corresponds to the maximum decomposition rate for the second step):

- for $E_a = 107\,\mathrm{kJ/mol}$, $k = 9.7 \times 10^{-4}\,\mathrm{s}^{-1}$
- for $E_a = 152\,\mathrm{kJ/mol}$, $k = 9.3 \times 10^{-4}\,\mathrm{s}^{-1}$

We have obtained different values of the reaction order by the non-isothermal constant heating rate and CRTA methods. In the classical non-isothermal method the reaction order which was obtained suggests the release of structural units consisting of one and two iodine molecules but a mass transfer limitation can alter the value of the reaction order. We note that in the CRTA procedure the limitations in mass transfer are lower than in the classical non-isothermal analysis.

It is important to note the agreement of the activation parameters between the classical nonisothermal technique (constant heating rate) and the CRTA technique:

- for the first step, both methods lead to a low value of the activation energy (< 40 kJ/mol)
- for the second step the activation energy is larger than 100 kJ/mol

These differences suggest two different iodine sites in the intercalated compound.

Conclusions

The present investigation has established that deintercalation of iodine from I-$Bi_2Sr_2CaCu_2O_{8+x}$ takes place in two steps which seems to indicate that two types of intercalated iodine exist in the 2212-I structure. Aproximatively 0.45 I is lost in the first deintercalation step with an activation energy which suggests *physical* desorption. The reaction order is n ~ 1. For the rest of the iodine, the decomposition is more likely of *chemical* nature, i.e. with higher activation energy (~ 150 kJ/mol).

The differential conversion function f(α) for the second decomposition stage is of the reaction order type.

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