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DETERMINATION OF TOTAL HETEROGENEITY AND FRACTAL DIMENSIONS OF HIGH-TEMPERATURE SUPERCONDUCTORS

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Abstract

Using thermo-analytical and sorptometric methods physicochemical properties and especially surface heterogeneity of $HgBa_2Ca_2Cu_3O_{8+\delta}$, (Hg-1223) was investigated. The desorption energy distribution was derived from mass loss Q-TG and differential mass loss Q-DTG curves of thermodesorption in quasi-isothermal conditions of pre-adsorbed *n*-octane and water vapour. It is shown that the superconducting Hg-1223 phase is highly sensitive to water vapours. The mechanism of water adsorption depends largely on the activation time. By water vapour saturation in a period of 90 min, physisorption takes place. Prolonged periods result in a chemical decomposition. From nitrogen ad- and desorption isotherms the fractal dimension of superconductors were calculated. A new approach is proposed to calculate fractal dimension from Q-TG curves.

Keywords: fractal dimension, heterogeneity, high-temperature superconductors, sorptometry, thermogravimetry

Introduction

Today, many electronic and energetic systems are based on superconducting oxides. Critical temperature T_c [1], critical current density J_c and critical magnetic field H_c, as well as surface properties limit technical applications of high-T_c oxides [2–5]. Current conductors, electromagnets, power cables, etc. more and more are equipped with an active superconductor centre.

A great number of physical and chemical processes take place or are initiated at the solid/gas or solid/liquid interface. The knowledge of the phenomena occurring there is of importance because in many cases they result in changes of the physicochemical properties of the material. One of the most striking property of a solid surface is its capability of adsorption of vapours and gases. It results from the fact that valences are only partially saturated on the crystal surface. Therefore, the solid surface can absorb molecules from gas, liquid and even solid phases. Thus, atmospheric

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gases such as H_2O and CO_2 may influence significantly the behaviour of superconducting oxides. Depending on the kind of material and other conditions one may observe different interaction of physical or chemical adsorption.

Literature [6] reports on different interactions of gases with CuO used as a model for complex high-T_c superconducting oxides. Water molecules may be chemisorbed strongly at low temperature, and captured dissociative between –145 and –115°C. At $YBa_2Cu_3O_{7-\delta}$, physical and chemical adsorption [7–9] or combinations are observed depending on temperature [8] and activation time [9]. Physical adsorption does not change the elementary composition of the surface layer. The chemically adsorbed multilayer of water molecules stimulates the exchange of ions between the surface and the bulk of the crystal lattice with simultaneous decomposition [7]. On $La_{2-x}Sr_xCuO_4$ water is chemisorbed [10] and on $Bi_2Sr_2Ca_2Cu_2O_{8+x}$ physisorbed [11]. Investigation of thermodesorption of water and nonpolar liquids on superconducting $HgBa_2Ca_2Cu_3O_{8+\delta}$ grains provides two kinds of information: influence of saturation time on the mechanism of adsorption of water molecules and quantitative description of the energetic heterogeneity of the surface [16, 17].

Adsorption behaviour, properties of the heterostructure and in particular the fractal dimension are necessary for understanding sorption and diffusion mechanisms in high temperature superconductors. The calculation of the fractal dimension may be obtained from measurements of adsorption, mercury porosimetry, scanning electron microscopy, small-angle X-ray scattering and nuclear magnetic relaxation. Sophisticated measuring techniques and disturbances e.g. by multilayer condensation complicate the necessary investigations. So far, only few studies those item are available.

For that reason, in this paper possibilities to study physicochemical properties of $HgBa_2Ca_2Cu_3O_{8+\delta}$ by means of thermal analysis and sorptometry are discussed. The Hg-1223 sample ($HgBa_2Ca_2Cu_3O_{8+\delta}$ material) is a higher member of the Hg homologous series [12, 13]. For example, $HgBa_2Ca_{(n-1)}Cu_nO_y$ (n=1, 2, 3) exhibits a maximum transition temperature of ~–140°C [14] and under a pressure of 150 kbar T_c= –120°C as detected by resistance measurements [15].

In the following we present for the first time a numerical and analytical procedure for the evaluation of total heterogeneity properties (desorption energy distribution and pore-size distribution) using sorptometry and thermodesorption of liquids from high-temperature superconductor surface under the quasi-equilibrium conditions. Moreover, a new method for the evaluation of fractal dimensions from Q-TG curve is proposed and discussed.

Experimental

We examined a Hg-1223 sample prepared by a solid-state reaction technique using reagent-grade HgO, BaO, CaO and CuO powders by means of a method described by Isawa *et al.* [18].

Thickness of the adsorbed liquid layers on the surface can be assessed by means of immersion of the solid sample. Adsorption of non-polar and polar liquid layers were measured using the Derivatograph Q-1500 D (MOM, Hungary). Classical thermogravimetric DTG curves of water were measured within a temperature range of 20 to 1000°C at a heating rate of 10° min^{-1}. The digitally recorded dynamic thermodesorption give the dependence of the sample mass loss as a function of temperature or time. Q-TG mass loss and Q-DTG differential mass loss curves were measured under the quasi-isothermal conditions in the temperature range 20–250°C at a heating rate of 6° min^{-1}.

Specific surface areas, pore size distribution and pore volume were calculated from low-temperature nitrogen adsorption-desorption isotherms measured by means of the Sorptomat ASAP 2405 V1.01 (Micrometrics).

Results and discussion

The Q-TG mass loss and Q-DTG differential mass loss of *n*-octane as a function of temperature from the Hg-1223 surface are presented in Fig. 1. The spectrum indicates two parts: a long wide peak with minimum near 125°C and another part with minimum at 140–200°C. Water thermodesorption (Fig. 2) shows one larger peak with a minimum near 100°C.

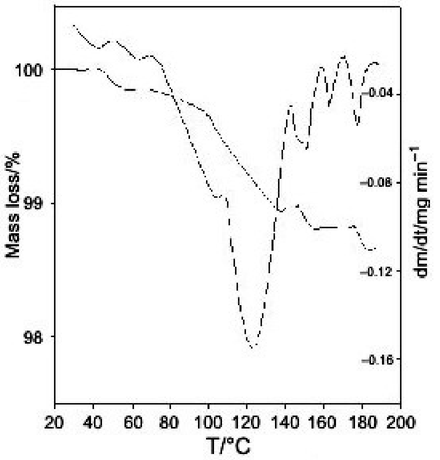

Fig. 1 Q-TG and Q-DTG curves of *n*-octane thermodesorption from Hg-1223 surface under quasi-isothermal conditions

The desorption energy distribution from Q-TG and Q-DTG curves was derived using an equation for the desorption kinetics characterised by a constant value of the desorption energy [17]:

$$-\frac{1}{1-\theta_i}\frac{d\theta_i}{dT}=\frac{\nu_i}{\beta}\exp\left(-\frac{E_i}{RT}\right) \tag{1}$$

where $T=T_o+\beta t$, θ the degree of surface coverage, ν the entropy factor, E_i the desorption energy calculated for each temperature, T_o and T the initial and given temperatures of desorption, respectively, β the heating rate of the sample, t the time and R the universal gas constant.

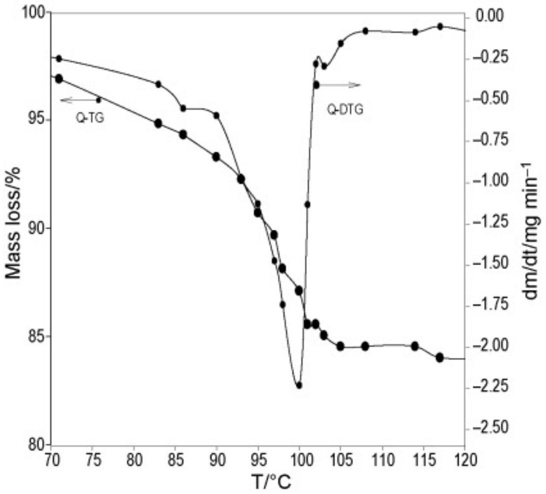

Fig. 2 Q-TG and Q-DTG curves of water thermodesorption from the Hg-1223 surface under quasi-isothermal condition

The final expression for determination of desorption energy distribution $\varphi_n(E)$ can be expressed in the form [17]:

$$\varphi_n(E) = -\frac{d\theta}{dT}\frac{1}{T} \tag{2}$$

Equation (2) was used for the calculation of desorption energy distributions from the pores for each temperature T_i in the Q-DTG curves (Figs 3 and 4). The distribution functions $\varphi_n(E)$ of *n*-octane and water desorption from the Hg-1223 surface

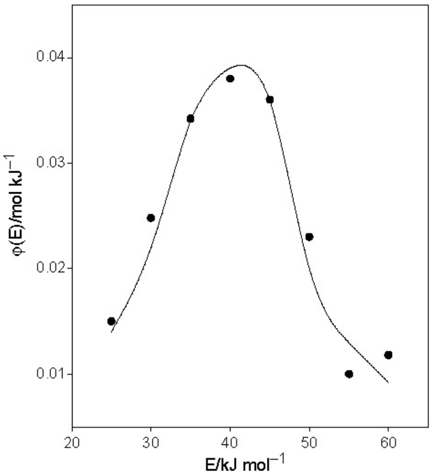

Fig. 3 Energy distribution function of *n*-octane desorption from the Hg-1223 surface calculated for the whole temperature range T=50–180°C

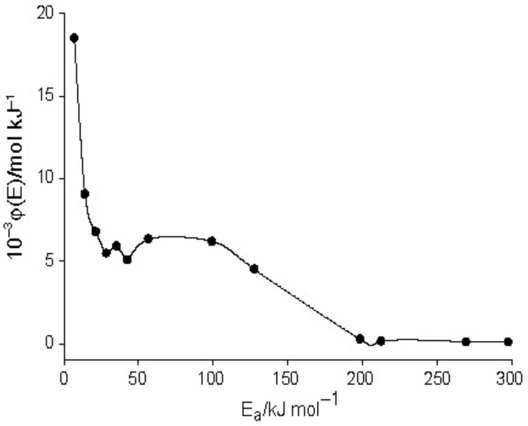

Fig. 4 Energy distribution function of water desorption from the Hg-1223 surface calculated for the whole temperature range T=50–180°C

within the temperature range T=50–180°C are represented in Figs 3 and 4. E_d values range from 28 to 60 kJ mol^{-1} and from 7 to 300 kJ mol^{-1}. In the case of water, the high value of desorption energy indicates a great influence of the surface molecules of the solid. The thermodesorption of *n*-octane and water shows that the investigated superconducting materials have a polar surface.

Figure 5 presents the evolution of DTG curves as a function of temperature for the of water from the Hg-1223 surface with preadsorbed vapour under classical (dynamic) conditions. The spectrum shows two parts: a wide peak with the minimum located near 100°C and another part with inflexion at 300–850°C. In the case of pure Hg-1223 (Fig. 5a) above ~440°C, a mass decrease was observed. The decomposition can be schematically described by the following equation [19]:

$$2HgBa_2Ca_2Cu_3O_y \leftrightarrow 2Hg(g)+(y-7-\delta')O_2+2Ba_2Cu_3O_{5+d'}+4CaO \qquad (3)$$

After a water vapour treatment within a period of $0<t_{act}<90$ min (Fig. 5b) an increase of a peak near 100°C is observed which corresponds to physical sorption. When the sample was kept in a dessicator longer than 90 min (Fig. 5c), weak peaks appear at 347, 375, 615°C, as well as at 410, 775°C when the activation is longer than 24 h (Figs 5e, 5f). It corresponds to the decomposition temperature of a product of the reaction of the sample with water. During longer treatment in water vapour of mercury superconducting oxide results in increasing peaks. The physical adsorbed water molecules stimulate the chemical process. After five days, a peak near 100°C decreases whereas other increases. This effect corresponds to a chemical reaction of water with the Hg-1223 surface.

A mean pore radius of 12.87 nm and a pore volume of 0.0039 cm^3 g^{-1} of the superconducting sample were calculated from desorption isotherms using the BJH method (Table 1). The BET specific surface area of the fresh ceramic material was 0.89 m^2 g^{-1}.

The low-temperature nitrogen adsorption-desorption isotherms presented in Fig. 6 were used for calculation of fractal dimension on the basis of a method pre-

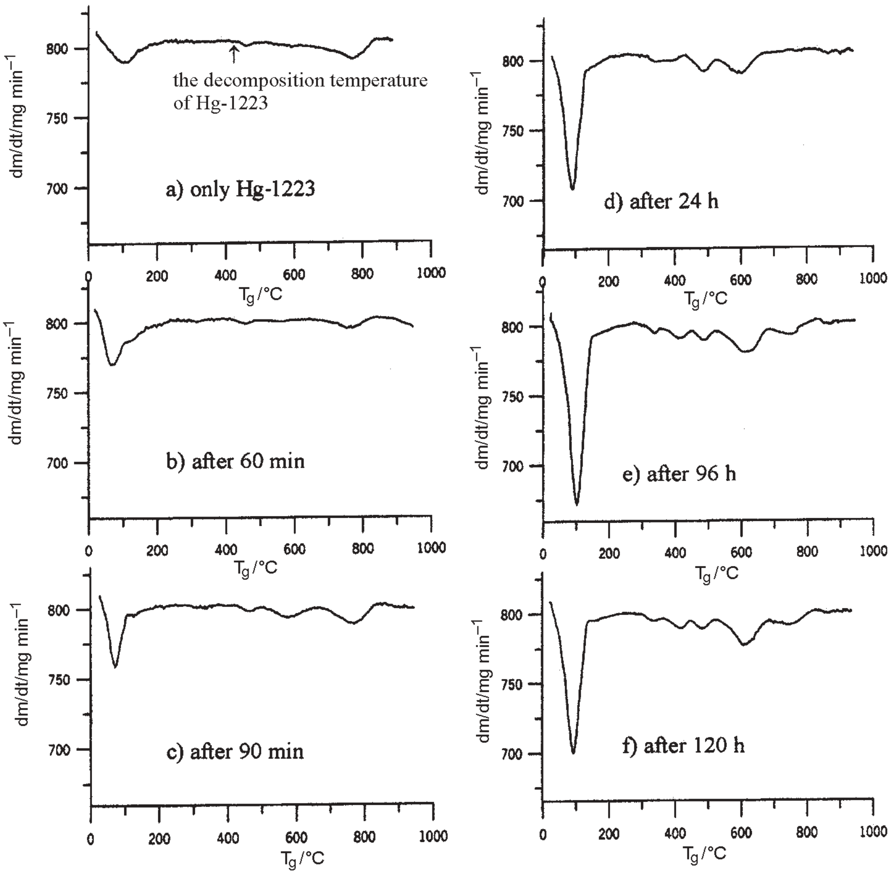

Fig. 5 Evolution of experimental of DTG curves as a function of temperature. Water vapour preadsorption on the Hg-1223 surface under dynamic conditions. The initial mass was 100 mg

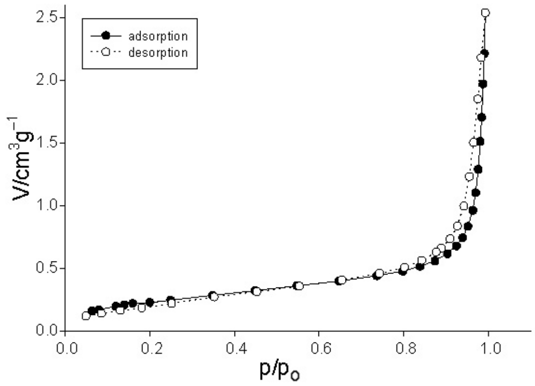

Fig. 6 Low-temperature nitrogen adsorption-desorption isotherms for Hg-1223

sented in paper [20]. This method is based on surface of the adsorbed layer calculated using Frenkel–Halsey–Hill theory and Kiselev equation [21]. The fractal dimension D can be calculated from relationships [22–24]:

$$D = 3 - \mathrm{d}[\ln a(x)]/\mathrm{d}[\ln(-\ln x)] \tag{4}$$

$$D = 2 + \mathrm{d}[\ln\int(-\ln x)\mathrm{d}a]/\mathrm{d}[\ln(-\ln x)] \tag{5}$$

$$\mathrm{d}V/\mathrm{d}r = A(r) \sim r^{(2-D)} \tag{6}$$

where a is adsorption value, x is section of the experimental isotherm, V and r are pore volume and radius, function $A(r)$ is determined from experimental data on sorption hysteresis.

Table 1 Pore structure parameters of $HgBa_2Ca_2Cu_3O_{8+\delta}$ sample calculated from nitrogen adsorption–desorption isotherms using sorptometric method

Parameter	Unit	Value
Single point surface area at p/p_o=0.2	$m^2\ g^{-1}$	0.80
BET surface area	$m^2\ g^{-1}$	0.88
Langmuir surface area	$m^2\ g^{-1}$	1.27
BJH adsorption cumulative surface area for 17.0000–3000.000 Å pores	$m^2\ g^{-1}$	0.91
BJH desorption cumulative surface area for 17.0000–3000.000 Å pores	$m^2\ g^{-1}$	0.93
Single point total pore volume for <780 Å pores	$cm^3\ g^{-1}$	0.028
BJH adsorption cumulative pore volume for 17.0000–3000.000 Å pores	$cm^3\ g^{-1}$	0.003
BJH desorption cumulative pore volume for 17.0000–3000.000 Å pores	$cm^3\ g^{-1}$	0.003
Average pore radius (4V/A by BET)	Å	128.7
BJH adsorption average pore diameter (4V/A)	Å	151.2
BJH desorption average pore diameter (4V/A)	Å	165.3

The pore size distribution was calculated from nitrogen adsorption-desorption data (Fig.6 and Table 1) obtained over pore size range 1.7–300 nm employning the Barrett-Joyner-Holenda (BJH) method. The pore size distribution curve (PSD) for Hg-1223 presented in Fig. 7 is of a Gaussian type with peak at pore radii ca. 20 nm.

Figures 8 and 9 present the dependencies ln$a$ as a function of ln(–ln$x$) (Fig. 8) and $\int(-\ln x)\mathrm{d}a$ as a function of ln(–ln$x$) (Fig. 9) using Eqs (4) and (5). The plots show a good linear relationship. Using above data the value of fractal dimensions were calculated to be 2.60 and 2.62, respectively.

The calculations of fractal dimension on the basis of Q-TG data presented in Fig. 1 was carried out as follows: First, the Q-TG mass loss curve was transferred in the form presented in Fig. 10. This figure shows the relationship between $\ln[(m_o - m_1)A]$ and $\ln[(m_1 - m_k)/\mathrm{d}]$, where: m_o is initial sample mass, m_1 is mass sample at temperature T_1, m_k is the final sample mass, d is density of n-octane and A is specific surface area of the superconductor. Point P is the intersection point of a and b

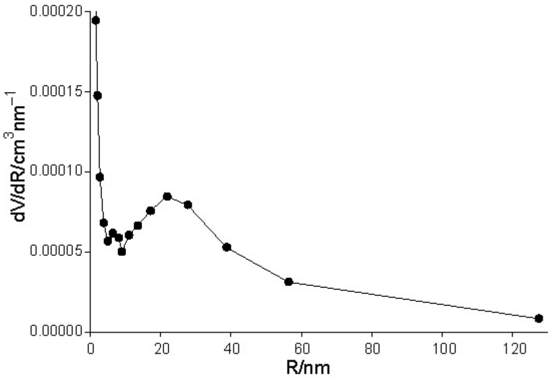

Fig 7 Pore-size distribution of Hg-1223

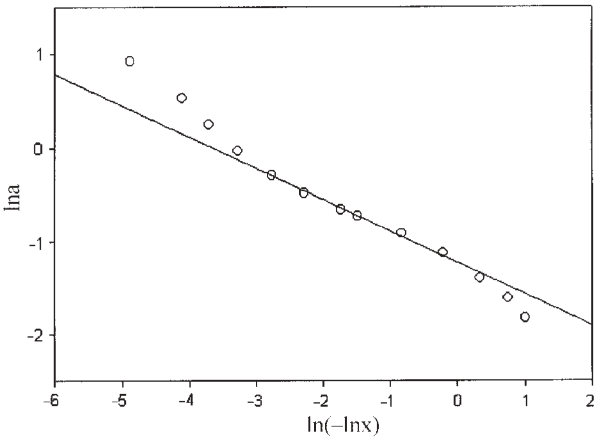

Fig. 8 Surface fractal dimension of Hg-1223 calculated from the adsorption isotherm

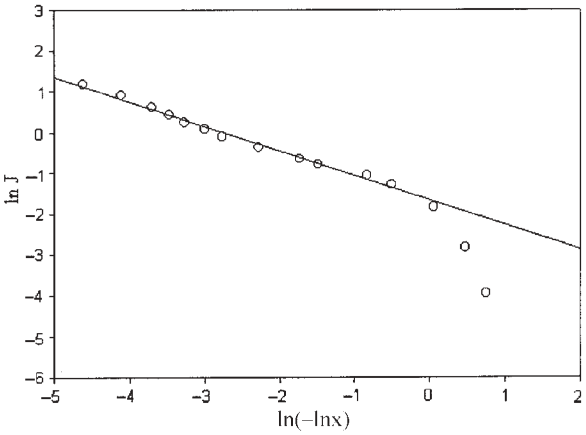

Fig. 9 Surface fractal dimension of adsorption Hg-1223 defined thermodynamically, $J=\int_a(-\ln x)\mathrm{d}a$

slopes and is related to point K in the curve presented in Fig. 10. The slop *c* is perpendicular to PK section and it was used to determination of *D* value. The point K is related to the minimum value of the differential mass loss in curve Q-DTG (Fig. 1). In our calculations the following equation was used for determination of the *D* value by the analytical method [25]:

$$D = (2+3k)/(1+k) \tag{7}$$

where *k* is the slope of *c* in Fig. 10.

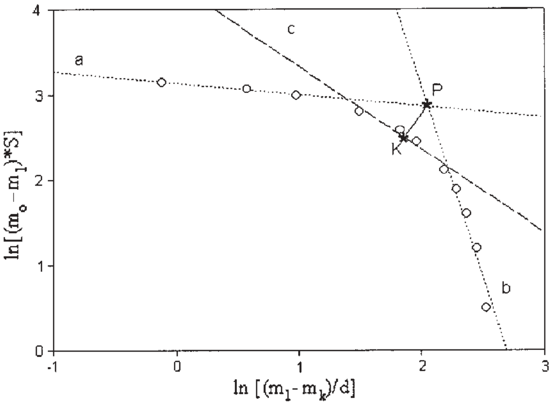

Fig. 10 Surface fractal dimension of Hg-1223 calculated on the basis of Q-TG thermodesorption of *n*-octane from under the quasi-isothermal conditions

The obtained fractal dimension value of D=2.49 calculated from thermodesorption measurements is in a good agreement with data determined from sorptometry and those given in the papers [26, 27].

Conclusions

We discussed special applications of thermal analysis for investigation of adsorbed liquid layers and of porosity parameters used for the quantitative characterisation of the energetic and structural heterogeneities of high-T_c oxide superconductor. The thermodesorption process of liquids depends on the surface wetting phenomenon and surface properties of the solid. The presented method is very useful to investigate physicochemical properties of surface liquid films, adsorbate-adsorbent interaction and total surface heterogeneity.

At room temperature, physical sorption and chemical reaction of H_2O on the oxide surface takes place. This phenomenon strongly depends significantly on the activation time t_{act} in a period $0<t_{act}<90$ min, physisorption was observed. In the case of longer water vapour action, $t_{act}>90$ min, a decomposing reaction was observed.

The new method for determination of the fractal dimension of superconductor surface using Q-TG technique is presented. It is in good agreement with results from low-temperature adsorption-desorption isotherms. The presented results show that above method for determination of the fractal dimension on the basis data thermodesorption of liquids in quasi-isothermal conditions is reliable, simple and practicable.

* * *

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