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STUDIES OF HETEROGENEITY PROPERTIES OF SELECTED HIGH-TEMPERATURE SUPERCONDUCTOR SURFACES

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Nitrogen adsorption measured at 77 K was used to characterize the surface heterogeneity of high-temperature superconductor surfaces. Properties relating to adsorption and porosity of the solids (adsorption capacity, specific surface area, radii and volume of the pores, pore-size distribution function) were determined from nitrogen adsorption–desorption isotherms and atomic force microscopy (AFM) for a series of oxide superconductors. It is shown that the adsorption isotherms of all samples are S-shaped and belong to type II according to the IUPAC classification. On the basis of the nitrogen adsorption isotherms and AFM data, fractal dimensions were determined and correlations found with adsorption and porosity parameters.

Keywords: *adsorption capacity, atomic force microscope, fractal dimension, high-temperature superconductor, porosity, sorptometry*

Introduction

A large number of physico-chemical processes take place and/or are initiated at solid/gas or solid/liquid interfaces. Knowledge of the phenomena occurring there is of importance because in many cases they result in changes in the physico-chemical properties of the material. One of the most striking properties of a solid surface is its capability of adsorption of vapours and gases. It results from the fact that valencies of atoms on the crystal surface are only partially saturated. Therefore, the solid surface can adsorb molecules from gas, liquid and even solid phases. Thus, atmospheric gases such as H_2O, N_2 and CO_2 may influence significantly the behaviour of materials of advanced technology. Depending on the kind of material and other conditions one may observe different interactions of physical and/or chemical adsorption. Adsorption behaviour, properties of the heterostructure and, in particular, the fractal dimensions are necessary for understanding sorption and diffusion mechanisms on nanosolid surfaces [1–3].

The main interest in superconductor materials, particularly in ceramic high-temperature superconductors, is due to their numerous potential applications [4–6]. The physico-chemical properties of superconductor surfaces are known only to a small extent. Due to their well-developed surface (larger specific surface area and presence of various active centres, which results in larger adsorption capacity), thin superconductor layers are more enriched in oxygen and are characterized by higher Curie temperature, T_c [7, 8]. Thin surface layers of various materials possess specific physical properties and for this reason they are applied in microelectronics in passive microwave devices, e.g. as high-quality resonators and low-loss filters. By using $YBa_2Cu_3O_{7-x}$ and $Tl_2Ba_2CaCu_2O_{8+x}$ type materials as thin layer circuits in passive microwave subunits, the conduction losses are dramatically reduced. Attributes such as small size, low mass and low losses make these subunits very desirable, not only for the communication systems used by NASA, but also in commercial telecommunication industry. Physico-chemical parameters such as, adsorption capacity and porosity, amongst others, can change the material's superconductor properties entirely by enhancing chemical reactions and can be responsible for the decomposition of the superconductor material [9].

The results obtained so far using quasi-isothermal thermogravimetry (Q-TG) show that the superconductors such as $YBa_2Cu_3O_{7-x}$ and $HgBa_2Ca_2Cu_3O_{8+x}$ are characterized by specific adsorption properties towards polar and nonpolar liquids (particularly water) and by porosity [10–12]. The specific surface area, pore size, pore volume and pore-size distribution functions are fundamental parameters for the characterization of solids. Properties such as porosity, strength, hardness,

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permeability, selectivity, corrosion, thermal stress resistance, etc. can be directly correlated to the porous structure of the materials. These properties can be easily investigated by physisorption techniques. For this reason, this paper presents a description of adsorption and porosity properties of chosen high-temperature superconductor surfaces, based on nitrogen adsorption–desorption isotherms, and AFM data.

Experimental

Three samples of high-temperature superconductors $La_{1.8}Sr_{0.2}CuO_4$, $SmBa_2Cu_3O_x$ and $Sm_{1.2}Ba_{1.8}Cu_3O_7$ were prepared by direct solid state reaction of oxides as reported earlier [12–14].

Nitrogen adsorption–desorption measurements at 77 K were carried out using an automatic ASAP 2405 V1.01 volumetric adsorption analyzer (Micrometrics Instrument Co., Norcross, GA, USA). The adsorption and porosity properties of the samples, as calculated from the adsorption isotherms, are listed in Table 1. Before the adsorption measurements, the samples were outgassed for 2 h at 473 K. In order to characterize fully the structural changes atomic force microscopy (AFM) (NanoScope III type, Digital Instruments, USA) was also used.

Results and discussion

Nitrogen adsorption-desorption isotherms measured at 77 K for the high-temperature superconductors are shown in Fig. 1. According to the IUPAC classification, isotherms of this kind are S-shaped and belong to the isotherms of type II describing the process of physical adsorption of nitrogen. The adsorption capacity, a, of samples has a range varying from 0.73 to 1.72 $cm^3\ g^{-1}$. The specific surface areas S_{BET} were calculated using the BET method [15] and were found to range from 0.63 to 1.83 $m^2\ g^{-1}$, with the corresponding total porosity varying from 0.001 to 0.0025 $cm^3\ g^{-1}$ (Table 1). The total pore volume and the pore-size distribution were calculated using the Barrett–Joyner–Halenda (BJH) method [16]. Figure 2 presents the pore-size distribution as the function $dV/dR=f(R)$, where V is the pore volume and R the pore radius. As can be seen, the pores with a radius near 2–4 nm have the highest value on these curves. The concentration of micropores decreases with increasing pore radius.

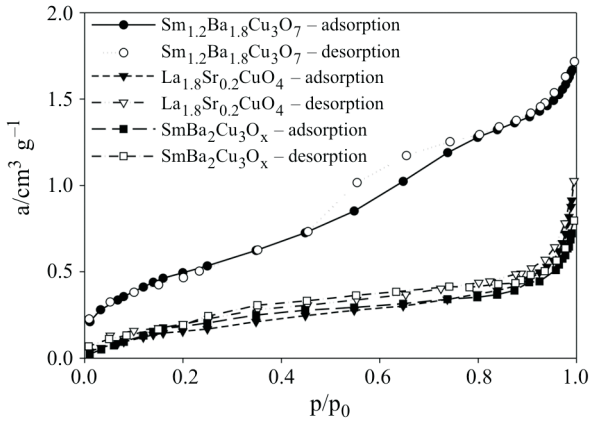

Fig. 1 Nitrogen adsorption–desorption isotherms (77 K) for studied samples

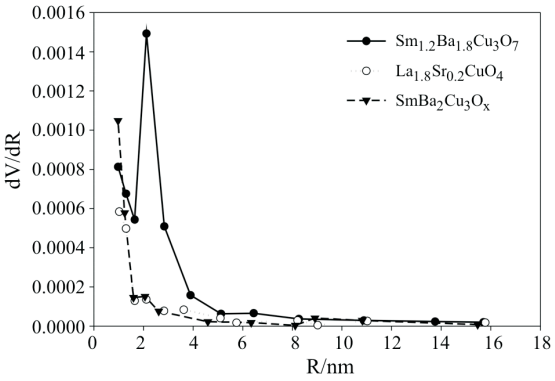

Fig. 2 Pore-volume distribution function for superconductor samples

The observed shape of the pore-size distribution curves is typical for most industrial mesoporous adsorbents. For example, this shape is similar to that evaluated from the low-temperature nitrogen adsorption isotherms for various activated carbons [17] using the Dollimore–Heal method [18]. The low-temperature nitrogen adsorption–desorption isotherms presented in Fig. 1 were used for the calculation of the fractal dimensions, based on the method presented in paper [12]. The fractal dimension characterizes the nature of adsorbents and heterogeneities of pores. This method is based on determining the sorption film surface, which can be calculated from the

Table 1 Adsorption and porosity parameters of superconductor samples determined from the nitrogen adsorption isotherms measured at 77 K

Sample	a_{max}/$cm^3\ g^{-1}$	S_{BET}/$m^2\ g^{-1}$	Pore volume/$cm^3\ g^{-1}$	Pore diameter/Å	a_m	C_{BET}
$Sm_{1.2}Ba_{1.8}Cu_3O_7$	1.72	1.83	0.0025	55.1	0.42	53.9
$La_{1.8}Sr_{0.2}CuO_4$	1.03	0.63	0.0013	79.9	0.14	21.1
$SmBa_2Cu_3O_x$	0.79	0.93	0.0010	43.1	0.21	9.53

Table 2 Fractal dimension values of the samples obtained from sorptometry and AFM data

Sample	Sorptometry	AFM	$D_{f(av.)}$
$Sm_{1.2}Ba_{1.8}Cu_3O_7$	2.36	2.76	2.56
$La_{1.8}Sr_{0.2}CuO_4$	2.29	2.61	2.45
$SmBa_2Cu_3O_x$	2.26	2.66	2.46

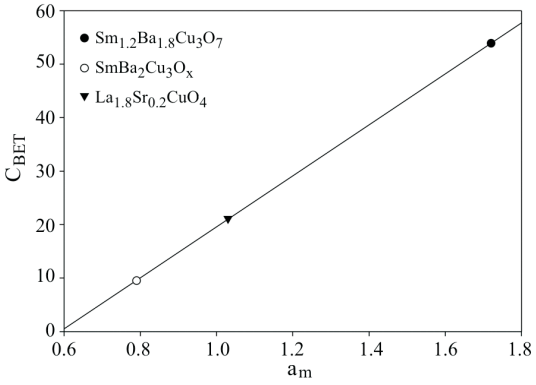

Fig. 3 Adsorption value of the constant C_{BET} *vs*. nitrogen monolayer a_m

Frenkel–Halsey–Hill theory and the Kiselev equation [19]. The fractal dimension D_f can be calculated from the relationships [20–24]:

$$D_f=3-d[\ln a(x)]/d[\ln(-\ln x)] \quad (1)$$

$$D_f=2+d[\ln\int(-\ln x)da]/d[\ln(-\ln x)] \quad (2)$$

where a is the adsorption value and x the section of the experimental isotherm.

Using above data the values of the fractal dimensions were calculated using Eqs (1) and (2). The average values and data obtained from AFM techniques are presented in Table 2.

Figure 3 shows the dependence of the adsorption value of the constant from the equation of BET theory, C_{BET}, on the monolayer of nitrogen adsorbed on the surfaces of superconductors, a_m. As seen from this relationship, a_m increases with increasing values of C_{BET}. The large C_{BET} value of the $Sm_{1.2}Ba_{1.8}Cu_3O_7$ is connected with the rapid formation of a thin adsorption layer of nitrogen on the surface. For small values of C_{BET}, a slow formation of a thick adsorption layer on the surface of the superconductor is observed. All superconductors studied here belong to the group of non-porous adsorbents [25, 26], as evidenced by the small specific surface areas ranging from 0.63 to 1.83 $m^2\ g^{-1}$ (Table 1).

The fractal coefficients of these materials increase from 2.26 to 2.36 (sorptometry data) and from 2.61 to 2.76 (AFM data). Figure 4 presents the AFM images of surfaces of superconductor samples. From the AFM data fractal coefficients were calculated using the method described in paper [27] and

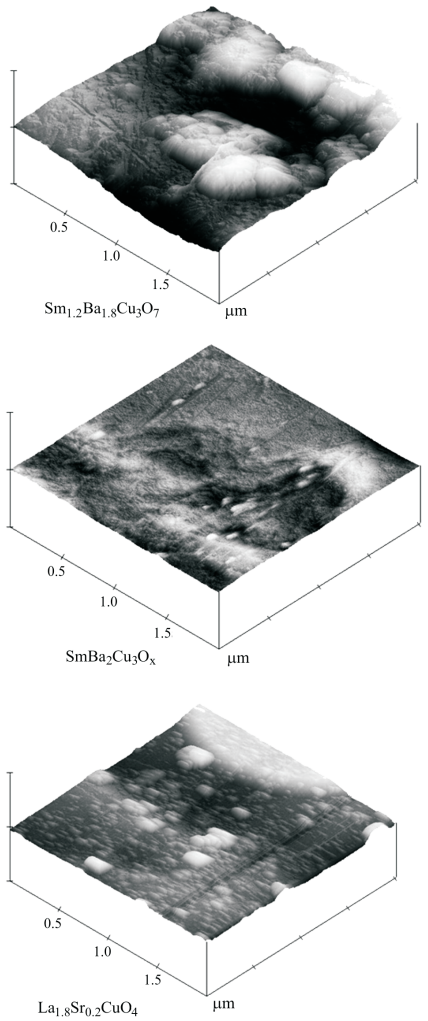

Fig. 4 AMF photographs of the sample surfaces

commercial software program in NanoScope III apparatus and presented in Table 2.

Figures 5 and 6 present relationships between the fractal coefficients and adsorption parameters. From these linear relationships it appears that fractal dimensions increase with increasing of S_{BET} and a_m values.

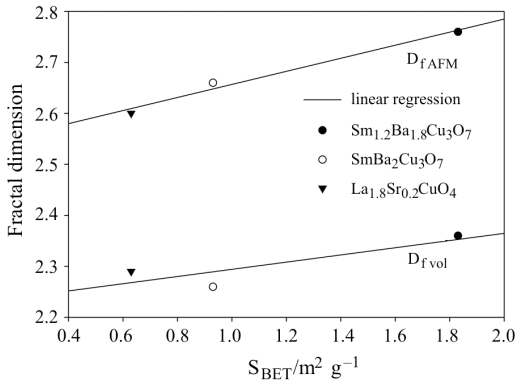

Fig. 5 Fractal dimensions calculated from sorptometry (vol) and AFM data as a function of surface area of samples

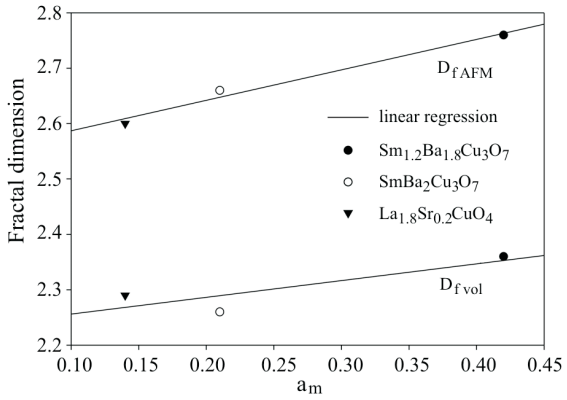

Fig. 6 Fractal dimensions calculated from sorptometry (vol) and AFM data as a function of adsorption values of monolayer

Conclusions

This paper presents results of investigations on adsorption and porosity of high-temperature superconductors using sorptometry and atomic force microscopy. Comparison of nitrogen adsorption–desorption data provides new information about the physicochemical properties of the surface of high-temperature superconductors. The ceramics studied here belong to the group of nonporous adsorbents with low specific surface areas and porosity. Sample surfaces possess micropores with a homogenous structure whose fractal coefficients are close to 2.5.

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