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STUDIES OF PHYSICO-CHEMICAL PROPERTIES AND FRACTAL DIMENSIONS OF SELECTED HIGH-TEMPERATURE SUPERCONDUCTOR SURFACES

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Properties relating to porosity of solids (fractal dimensions, surface roughness parameters) were evaluated from atomic force microscopy (AFM) and nitrogen adsorption-desorption isotherms measured at 77 K for selected high-temperature [(RE) $Ba_2Cu_3O_{7-x}$, *RE*=Y, Sm] superconductors. Adsorption capacity, specific surface area, fractal dimensions were determined from adsorption-desorption isotherms. The adsorption isotherms of all samples were S-shaped and belong to type II according to the IUPAC classification. A linear relationship was demonstrated between the fractal coefficients calculated by using the two methods and values of adsorption capacity of monolayer.

Keywords: *adsorption-desorption isotherms, atomic force microscopy, fractal dimensions, high-temperature superconductors, surface roughness parameters*

Introduction

The surface resistance (R_s), below superconducting transition temperature T_c, of the high-temperature superconductors (HTS) is approximately two or three orders of magnitude smaller than that of conducting metals usually used in the microwave-frequency region. High-temperature superconducting $YBa_2Cu_3O_{7-x}$ (YBCO) [1–24] and $Tl_2Ba_2CaCu_2O_{8+x}$ [2, 25] thin films with low microwave surface resistance R_s are suitable candidates for passive microwave devices, such as high-Q resonators, low loss filters that can be used for satellite [1–4] and mobile communication systems [5–11]. The development of HTS microwave devices requires high quality HTS thin films deposited on both sides of suitable low dielectric loss tangent substrates, such as sapphire [1, 9, 12–14], magnesium oxide MgO [2, 3, 7, 8, 10, 12, 15–18, 22], perovskites ($LaAlO_3$ [1–3, 5, 11, 19–21], $SrTiO_3$ [22, 23], $BaZrO_3$ [23], $KTaO_3$ [24]). Moreover, the wafers available for HTS filters usually have a maximum size of only 50 or 75 mm.

Thus, the filters required are often quite complex with perhaps 12 or more resonators in a wafer. The dielectric resonator, especially the HTS/sapphire resonator, has become the standard characterization technique to measure the R_s of HTS samples at low *RF* power levels [26]. Dielectric resonators can work in the Transverse Electric (TE) modes, Transverse Magnetic (TM) as well as in Hybrid modes denoted variously as HEM, EH or HE; including Whispering Gallery modes. Microwave characterization of superconductors using dielectric resonators is typically done in the TE_{011} mode (as this mode is insensitive to electrical contacts on a circular concentric path) and measurements are performed using the Hakki-Coleman, open ended or Whispering Gallery mode structures [27].

A significant reduction in size and mass of filters can be achieved with the use HTS technology. HTS filters also offer improvement in the insertion loss. The unloaded quality factor Q_u of a microwave resonator in general can be written as $Q_u=(R_s/G+F\tan\delta)^{-1}$, where G is a factor determined by the resonator's geometry, which typically increases as the resonator dimensions increase, while F is a factor determined by the fraction of the electrical energy of the cavity stored in the dielectric materials. R_s is the surface resistance and $\tan\delta$ is the loss tangent of the dielectric material. It is clear that the unloaded Q_u can be increased by reducing either R_s or $\tan\delta$ or both. The residual surface resistance of HTS materials originates most probably from the presence of defects that act as scattering centres in these advanced materials. Surface roughness, grain boundaries, dislocation in growth terraces, screw dislocations, oxygen vacancies, OH^- ions, impurities have been suggested as possible sources of defects [16, 28]. A great number of

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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 important because in many cases they result in changes of the physicochemical properties (e.g. adsorption and porosity) of the material. One of the most striking property of solid surface is its capability of adsorption of vapour and gases. It results from the fact that valences of atoms on the crystal surface are only partially saturated. Therefore, the solid surface can absorb molecules from gas and/or liquid and even solid phases. It is well known that the substitution of yttrium in $YBa_2Cu_3O_{7-x}$ by a rare earth (RE) element leads to a homologous superconducting (RE123)-compound with T_c rising with increasing ionic radius of the rare earth (RE) element. Studies of the relationship between T_c and oxygen content, as well as orthorhombic-to-tetragonal phase transition have concluded that the RE123s of larger RE ionic size have higher entropy, and oxygen is more disordered than for the smaller RE123s [29–32]. In the group [$(RE)Ba_2Cu_3O_{7-x}$, *RE*=Y, Er, Sm)] Sm123 has the least anisotropic pinning characteristics which makes it a good candidate material for various high power applications [33].

In this paper we report characterization of selected high-temperature [$(RE)Ba_2Cu_3O_{7-x}$, *RE*=Y, Sm] superconductors and analysis of their surface morphology and microstructure, based on atomic force microscope (AFM) data and compare surface porosity properties determined earlier from nitrogen adsorption-desorption isotherms [34, 35].

Experimental

The samples of [$(RE)Ba_2Cu_3O_{7-x}$, RE= Y, Sm] superconductors were prepared by direct solid-state reaction using oxides of at least 99.99% purity. The first and second calcinations were carried out at 1203 and 1243 K for 24 h, each with intermittent grinding at 873 K for 24 h in oxygen flow. The powder samples were then ground and pressed into pellets. The oxygen contents were measured by iodometric titration with reproducibility of at least 0.02. 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. The resistivity was measured using a four-point probe method in a liquid helium dewar.

Thermogravimetric analyses (TG) were performed by using a Cahn RG (USA) ultra-microbalance system with heating in vacuum and controlled environments at rate of 10 K min^{-1} in order to study mass uptake or loss at higher temperatures.

Nitrogen adsorption-desorption measurements at 77 K were carried out using an automatic ASAP 2405 V1.01 volumetric adsorption analyzer (Micrometrics Instrument Corp., 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. The surface morphology was examined by atomic force microscopy (AFM) (NanoScope III type, Digital Instruments, USA).

Results and discussion

Nitrogen adsorption-desorption isotherms measured at 77 K for the high-temperature superconductors were shown in papers [34, 35]. According to the IUPAC classification, isotherms of this kind are S-shaped and belong to type II describing the process of physical adsorption of nitrogen. The specific surface areas S_{BET} were calculated using the BET method [36] and were found to range from 0.34 to 1.88 $m^2\ g^{-1}$ 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 Barret-Joyner-Halenda (BJH) method [37]. The low-temperature nitrogen adsorption-desorption isotherms were used for the calculation of the fractal dimensions, based on the method presented in paper [34]. 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 Frenkel-Halsey-Hill theory and the Kiselev equation [38].The fractal dimension D_f can be calculated from the relationships [39–42]:

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

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

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

From obtained 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. The fractal dimensions (D_f) of these materials increase from 2.26 to 2.36 (sorptometry data) and from 2.66 to 2.76 (AFM) data. Figure 1 presents the AFM images of surface superconductor samples. The AFM photograph scanned an area of 1000·1000 nm. The surfaces of samples were heterogeneous. Sm123 sample has more point defects than Y123 due to oxygen disorder and the substitution of Sm for Ba. Further studies are needed to understand the microscopic, structural and chemical differences among RE123 samples.

Table 1 Adsorption and porosity properties of the high-temperature superconductor samples determined from the nitrogen adsorption isotherms

Sample	Specific surface area S_{BET} /m^2 g^{-1}	Total pore volume V/cm^3 g^{-1}	Adsorption value for monolayer a_m/mmol g^{-1}	Pore diameter/nm	Constant C_{BET}
$YBa_2Cu_3O_{7-x}$	0.34	0.0019	0.22	6.882	8.03
$SmBa_2Cu_3O_{7-x}$	0.93	0.0010	0.21	4.31	9.53
$Sm_{1.2}Ba_{1.8}Cu_3O_7$	1.83	0.0025	0.42	0.42	53.9

Table 2 Fractal dimension values and surface roughness parameters of the high-temperature superconductor samples determined from sorptometry and AFM data

Sample	D_f Sorptometry	D_f AFM	S_a/nm	S_{ku}
$YBa_2Cu_3O_{7-x}$	2.31	2.74	12.6	3.76
$SmBa_2Cu_3O_{7-x}$	2.26	2.66	1.66	2.44
$Sm_{1.2}Ba_{1.8}Cu_3O_7$	2.36	2.76	28.1	2.93

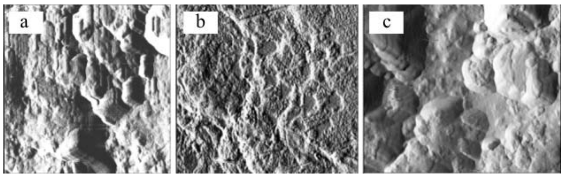

Fig. 1 AFM photographs of the surfaces (RE)$Ba_2Cu_3O_{7-x}$ samples: a – $Y_1Ba_2Cu_3O_{7-x}$, b – $Sm_1Ba_2Cu_3O_{7-x}$, c – $Sm_{1.2}Ba_{1.8}Cu_3O_7$

The fractal dimensions were calculated on the basis of Fourier transformation from AFM images using commercial software Scanning Probe Image Processor (SPIP).

The roughness average (S_a) and the surface kurtosis (S_{ku}) were determined from the dependence:

$$S_a=1/MN\Sigma\Sigma|z\ (x_k,y_l)-\mu| \qquad (3)$$

$$S_{ku}=1/MMS_q^4\Sigma\Sigma[z(x_k y_l)-\mu]^4 \qquad (4)$$

where S_{ku} describes the peak-less of the surface topography, for Gaussian height distribution S_{ku} approaches 3.0 when increasing the number of pixels. Smaller values indicate broader height distribution and vice versa for values greater than 3.0, μ is the mean height:

$$\mu=1/MN\Sigma\Sigma z\ (x_k,y_l) \qquad (5)$$

z – local height, MN – analyzed area of the surface. S_q – the root mean square, is defined as:

$$S_q=(1/MN\Sigma\Sigma[z\ (x_k,y_l)-\mu]^2)^{1/2} \qquad (6)$$

With increasing D_f values, an increase of surface heterogeneity of superconductor samples is observed. Figure 2 present relationships between the fractal dimensions and adsorption values of monolayer (a_m). From these linear relationships it appears that fractal dimensions increase with increasing a_m values.

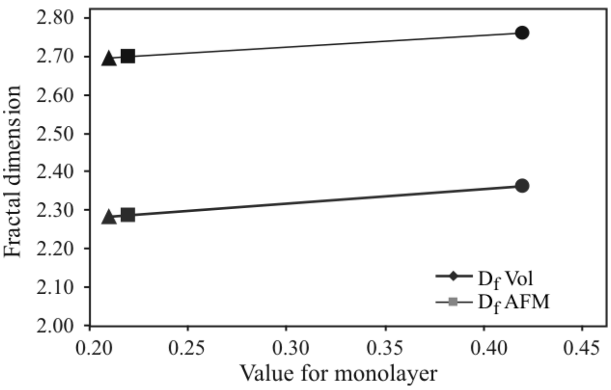

Fig. 2 Fractal dimensions calculated from sorptometry D_f vol and D_f_AFM data *vs*. adsorption value of monolayer a_m

Conclusions

We have studied three different high-T_c cuprates as a function of doping. This paper presents results of investigation on porosity of high-temperature superconductors using sorptometry and atomic force microscopy. The ceramics studied here belong to the group of nonporous adsorbents with specific surface areas from 0.34 m^2 g^{-1} for $YBa_2Cu_3O_{7-x}$ to 1.83 m^2 g^{-1} for $Sm_{1.2}Ba_{1.8}Cu_3O_7$. It has been demonstrated that with increasing fractal dimensions (D_f) values an increase of surface heterogeneity of superconductor samples is observed.

The results of the fractal dimensions of superconductor surfaces determined on the basis of sorptometry and AFM data are in quite good agreement and are close to 2.5.

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