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# CHARACTERIZATION OF PHYSICO-CHEMICAL PROPERTIES OF THE HIGH-TEMPERATURE SUPERCONDUCTOR AND $LaCoO_3$ SURFACES

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## Abstract

This paper presents possible applications of thermal analysis and sorptomatic methods to study physico-chemical properties of the high-$T_c$ superconductor $Y_1Ba_2Cu_3O_{7-x}$ and perovskite $LaCoO_3$. It is shown that both $Y_1Ba_2Cu_3O_{7-x}$ and perovskite phase are highly sensitive to water vapour. Mechanism of adsorption of water on $LaCoO_3$ depends largely on time activation ($t_{act}$). When the time of water vapour saturation was $0<t_{act}<180$ s, physisorption process was observed. In the case of longer times water vapour action, $t_{act}>180$ s, chemical decomposition was observed.

**Keywords:** fractal dimensions, high-temperature superconductor, perovskite, surface properties

## Introduction

During the last several years of high-temperature superconductivity (HTS) research there are many activities on applications in communication systems [1]. Microwave HTS technologies have been regarded as emerging technologies for mobile telecommunications [2–5], as well as for satellite communications [6–9].

HTS materials showed, below critical temperature, low surface resistance ($R_s$), at microwave frequency regions, ranged from 20 to 50 mΩ (at 14.5 GHz, 75 K). $Y_1Ba_2Cu_3O_{7-x}$ (YBCO) thin films deposited on low dielectric loss substrates such as perovskites ($LaAlO_3$ [2, 4, 5, 7, 8, 10–12], $SrTiO_3$ [13], $BaZrO_3$ [14]), MgO [4, 5, 7–9, 15, 16], sapphire [6, 17] have been used for fabricating microwave subunits such as high-$Q$ resonators and low-loss filters. The surface resistance $R_s$ of HTS, below critical temperature, is 1000 times lower than normal metals at 2 GHz and 60 K, the $Q$ factor of microstrip resonator using HTS film is approximately $1\cdot10^5$, much higher than the ordinary resonator, and the filter with these resonators has very

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good performance. Superconductors, as opposed to conventional conductors, have the ability to conduct electrical current with very small resistance, no power loss, no generation of heat, and greatly reduced levels of noise.

The quality control of HTS filters include two of the important control parameters: the $R_s$ of HTS films and homogeneity in the microwave properties of large HTS films.

Studies have been performed to measure the $R_s$ of HTS films by using dielectric-loaded resonator method, which has been accepted as a standard measurement method for the $R_s$ of HTS films [18].

The residual surface resistance of HTS originates most probably from the presence of defects [13] that act as scattering centers in these materials. Defects can be punctual like oxygen vacancies or impurities such as $OH^-$ ions [16] but granularity of the films is likely to be considered as an extended defect.

The physico-chemical properties of the high-$T_c$ superconductor and perovskite surfaces are known only to a small extent.

Physico-chemical parameters such as adsorption capacity and porosity can change the materials superconducting properties entirely by enhancing reactions and can be responsible for the decomposition of the superconducting materiaL [19]. The results obtained so far show that the superconductor $Y_1Ba_2Cu_3O_7$ is characterized by specific adsorption properties towards polar and apolar liquids (particularly water) and porosity.

The specific surface area, pore size, pore volume and pore-size distribution functions are fundamental parameters for characterization of solids. Properties such as porosity, strength, hardness, 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.

The microgravimetric method is very useful in analysis of oxide superconductors, because it enables investigations in vacuum and controlled environments [20, 21] in applications: thermogravimetric analysis for the study of solid-state reactions, kinetic and thermodynamic of reactions [22], determination of oxygen content in redox reactions, adsorption and surface properties these materials [19], and coupled techniques, for example TG-DTA, TG-MS, etc..

Knowledge of the chemistry and thermodynamics of the oxides is essential not only for prediction of the optimum processing conditions for the different forms of the materials, but also for understanding of the origins of defects.

In this paper we review our earlier obtained results for $Y_1Ba_2Cu_3O_{7-x}$ and describe physico-chemical and structural properties of perovskite $LaCoO_3$ for comparison their surface properties. An attempt was made to determine stability of studied compounds as far as the contact with water vapour is concerned using the thermal analysis methods.

## Experimental

The sample of high-temperature superconductor $Y_1Ba_2Cu_3O_{7-x}$ was prepared by direct solid-state reaction using oxides as described in [19]. The first and second calcinations were carried out at 1203 and 1243 K, each for 24 h, with intermediate grinding at 873 K for 4 h in an oxygen flow. The powder samples were then ground and pressed into rectangular pellets of a size suitable for resistivity measurements. The pellets were sintered in an oxygen flow at 1253 K for 20 h and then the furnace was cooled to room temperature.

Synthetic perovskite of the chemical composition $LaCoO_3$ was prepared by calcination for 3 h at 1473 K. Low-temperature nitrogen adsorption–desorption at 77 K was measured using an automatic ASAP 2405 volumetric adsorption analyzer (Micrometric Co. USA).

The specific surface area, radii and pore volume were calculated from the obtained adsorption-desorption isotherms as well as fractal dimensions. Thermogravimetric analyses (TG) were performed by using Cahn RG (USA) ultra-microbalance system [23] with heating in dynamic vacuum in order to study of oxygen loss from $Y_1Ba_2Cu_3O_{7-x}$. Studies of water thermodesorption were performed with simultaneous derivatograph Q-1500 D [24] over the temperature range from 293 to 1273 K with a furnace-heating rate of 10 K $min^{-1}$. The TG and DTG curves were registered digitally under the control of the program Derivat running on PC.

The samples were characterized by powder X-ray diffraction using a Stadi P (Stoe) diffractometer with a position-sensitive detector operating with $CuK_\alpha$ radiation. X-ray examination of $Y_1Ba_2Cu_3O_{7-x}$ revealed that the synthesis was essentially complete after the first heating. XRD pattern of $LaCoO_3$ showed occurrence of a distinguish, wide peak coming from an amorphous substance and visible sharp peaks corresponding to the structure $LaCoO_3$ (trigonal arrangement, according to the new nomenclature-hexagonal, the spatial group R-32/m). The calculated lattice constants for the studied material are: $a$=5.4501 A and $c$=13.0969 A. Studies showed the oxygen deficit in the $LaCoO_{3-y}$.

## Results and discussion

Nitrogen adsorption isotherms measured at 77 K for the high-temperature superconductor $Y_1Ba_2Cu_3O_{7-x}$ are shown in [25] and for $LaCoO_3$ are presented in Fig. 1. Isotherms of this kind are S-shaped and belong to the isotherms of type II describing the process of physical adsorption of nitrogen.

The specific surface areas were calculated using the BET method [26] and were found to range from 0.34 to 1.45 $m^2\ g^{-1}$ with the corresponding total porosity varying from 0.0019 to 0.003 $cm^3\ g^{-1}$. The total pore volume and pore-size distribution were calculated using the Barrett–Joyner–Halend (BJH) method [27]. Table 1 presents the

**Table 1** Adsorption and porosity properties of $Y_1Ba_2Cu_3O_{7-x}$ and $LaCoO_3$ samples determined from the nitrogen adsorption isotherms

| Sample | $S_{BET}$/ $m^2\ g^{-1}$ | Total pore volume/ $cm^3\ g^{-1}$ | Pore diameter/ Å | $a_m$/ mmol $g^{-1}$ | Constant/ $c_{BET}$ |
|---|---|---|---|---|---|
| $Y_1Ba_2Cu_3O_{7-x}$ [25] | 0.34 | 0.0019 | 68.82 | 0.22 | 8.03 |
| $LaCoO_3$ | 1.45 | 0.003 | 69.7 | 0.32 | 14.47 |

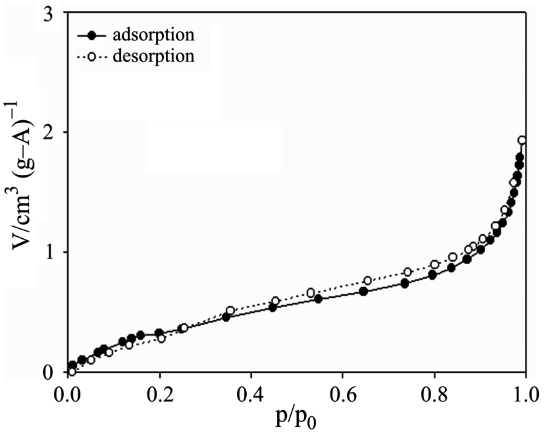

**Fig. 1** Nitrogen adsorption–desorption isotherms (77 K) for $LaCoO_3$ sample

structural-adsorption parameters of $Y_1Ba_2Cu_3O_{7-x}$ and perovskite. The studied materials belong to the group of mesoporous adsorbents as indicated by the small specific surface area 1.45 m$^2$ g$^{-1}$.

The low-temperature nitrogen adsorption-desorption isotherms presented in [25] and in Fig. 1 were used for calculation of the fractal dimensions, based on the method presented in [28]. The fractal dimension characterizes the nature of sorbents and the 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 [29]. The fractal dimension $D_f$ can be calculated from the relationships [30–32]:

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

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

$$D_f=2+n_f \quad (3)$$

where $a$ is the adsorption value, $x$ the section of the experimental isotherm, and $n_f$ is the fractional part. The values of the fractal dimensions were calculated by the analytical method (Table 2).

**Table 2** Fractal dimentions of the sorbents obtained from Eqs (1)–(3) and the average values

| Sample | $D_{f1}$ | $D_{f2}$ | $D_{f3}$ | $D_{f\,\mathrm{average}}$ |
|---|---|---|---|---|
| $Y_1Ba_2Cu_3O_{7-x}$ [25] | 2.31 | 2.31 | 2.30 | 2.31 |
| $LaCoO_3$ | 2.21 | 2.31 | 2.30 | 2.27 |

Kinetic of oxygen loss from chain position in the elementary cell of $Y_1Ba_2Cu_3O_{7-x}$ [33] was studied in dynamic vacuum and described earlier [33]. It is important in view of the high oxygen diffusion coefficient in this cuprate [34]. The process of oxygen loss from the chain positions was characterized by activation energy of 0.92±0.02 eV.

The results of TG and DTG analysis of water thermodesorption from a sample $Y_1Ba_2Cu_3O_{7-x}$ are presented in [19]. From the data presented it is clear that there are two peaks in the DTG curve corresponding to the desorption of water. The calculated data reveal that $Y_1Ba_2Cu_3O_{7-x}$ is characterized by a large adsorption capacity. The degradation of YBCO surface in water is observed to form nonsuperconducting hydroxides and carbonates.

Figure 2 presents the changes of DTA curves in the function of water vapour preadsorption registered for different times of water vapour contact with the perovskite sample. The data of thermal analysis carried out by the dynamic method showed that the studied material $LaCoO_3$ shows stability in the water vapour atmosphere in the time $t<180$ s (Fig. 2). Then it reacts with water which is indicated by the exothermal peak at about 573 K (300°C) for the sample saturated with water vapour for 3 min compared to the unmodified spectrum of $LaCoO_3$. Due to a longer contact ($t>10$ min), there appears an additional peak with the maximum at about 753 K (480°C) indicating developing decomposition and change of mechanism.

It is by now well known that the surfaces of high temperature superconductor (HTS) materials not representative of the bulk, primarily due to degradation in air, and especially with exposure to moisture, and some form of surface cleaning is necessary to many applications. The problem of surface degradation is exacerbated by short superconducting coherence lengths in cuprate superconductors, e.g.~2–15 A for YBCO.

Water is typical atmospheric contamination which can modify surface properties YBCO thin films deposited on low dielectric loss substrates. The quality of the films, at microwave frequencies, is assessed on the basis of surface resistance of the

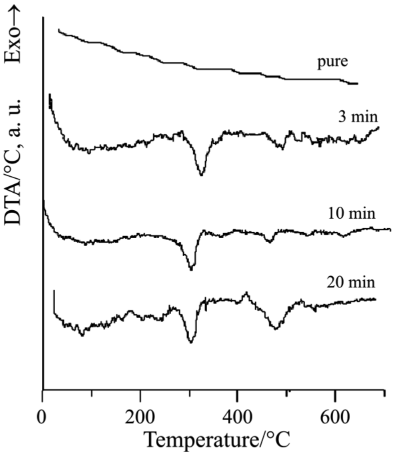

**Fig. 2** Evolution of experimental differential mass loss *Q*-DTA curves in relation to the temperature for the preadsorbed vapour of water on the $LaCoO_3$ surface under so-called dynamic conditions. The initial mass of the sample was 100 mg

material. Residual surface resistance of high temperature superconductors originates from the presence defects like oxygen vacancies or impurities such as $OH^-$ ions that act as scattering centers in these materials. HTS filters offer size and mass reduction and improvement in the insertion loss. The unloaded $Q$ 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 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 reducting either $R_s$ or $\tan\Delta$ or both of them.

## Conclusions

This study discusses the special use of the thermal analysis data on preadsorbed water vapour and porosimetry parameters for the quantitative characterization of the energetic and structural heterogeneites of high-$T_c$ oxide and perovskite surfaces.

Thermodesorption process of liquid depends on the surface wetting phenomenon and surface properties of the solids studied. The presented method is very useful to investigate physico-chemical properties of surface liquid films, adsorbate-adsorbent interaction and solid heterogeneity. The programmed thermodesorption investigations of the liquids [19] have provided evidence that the $Y_1Ba_2Cu_3O_{7-x}$ has a polar surface. The high-$T_c$ superconductor samples display a very large affinity for the adsorption of polar liquids. The adsorption of water molecules destroys the porosity of the surface. This is stimulated by electric fields in ordering the water dipoles in the multilayers. YBCO samples have only one kind of pores, as confirmed by sorptomatic measurements.

At room temperature, physical sorption and chemical reaction of $H_2O$ on the $LaCoO_3$ surface took place. This phenomenon depends significantly on time activation ($t_{act}$). When $t_{act}$ was $0<t_{act}<180$ s physisorption was observed. In the case of longer water vapour action, $t_{act}>180$ s the decomposition reaction was found. The XRD studies showed oxygen deficit in the structure of the compound under discussion.

## References

1 R. R. Mansour, IEEE Trans. Microwave Theory Tech., 50 (2002) 750.

2 J. S. Kwak, J. H. Lee, J. P. Hong, S. K. Han, W. S. Kim and K. R. Char, IEEE Trans. Appl. Supercond., 13 (2003) 17.

3 B. A. Willemsen, IEEE Trans. Appl. Supercond., 11 (2001) 60.

4 J. S. Hong, M. J. Lancaster, D. Jedamzik, R. B. Greed and J. G. Mage, IEEE Trans. Microwave Theory Tech., 48 (2000) 1240.

5 B. Marcilhac, Y. Lemaitre, D. Mansar and J. G. Mage, IEEE Trans. Appl. Supercond., 9 (1999) 4014.

6 M. Klauda, T. Kasser, B. Mayer, Ch. Neumann, F. Schnell, B. A. Aminov, A. Baumfalk, H. Chaloupka, S. Kolesov, H. Piel, N. Klein, S. Schornstein and M. Bareiss, IEEE Trans. Microwave Theory Tech., 48 (2000) 1227.

7 E. R. Soares, J. D. Fuller, P. J. Marozick and R. L. Alvarez, IEEE Trans. Microwave Theory Tech., 48 (2000) 1190.
8 R. Romanofsky, J. D. Warner, S. A. Alterowitz, L. Covey, A. Smith, P. Newman and K. G. Duh, IEEE Trans. Microwave Theory Tech., 48 (2000) 1216.
9 E. Polturak, G. Koren, I. Flohr, R. Waller and M. Guelman, IEEE Trans. Microwave Theory Tech., 48 (2000) 1289.
10 D. Seron, H. Kokabi, M. Rabii, S. Sautrot and G. Alquie, J. Supercond., 16 (2003) 857.
11 B. W. Tao, Y. R. Li, X. Z. Liu, M. He and J. Geerk, J. Vac. Sci. Technol. A, 20 (2002) 1898.
12 K. Chen, M. J. Chen, J. H. Chen, H. Ch. Yang, L. M. Wang, Ch. Y. Huang and B. Wang, IEEE Trans. Appl. Supercond., 11 (2001) 4010.
13 Y. C. Fan, A. G. Fitzgerald and J. A. Cairns, J. Vac. Sci. Technol. B, 18 (2000) 2377.
14 T. Watanabe, Y. Ohashi, T. Maeda, M. Mimura and I. Hirabayashi, IEEE Trans. Appl. Supercond., 13 (2003) 2484.
15 Y. B. Zhu, J. W. Xiong, S. F. Wang, Y. L. Zhou, Q. Zhang, S. Y. Dai, Z. H. Chen, H. B. Lu and G. Z. Yang, J. Supercond., 16 (2003) 967.
16 M. A. Hein, R. G. Humphreys, P. J. Hirst, S. H. Park and D. E. Oates, J. Supercond., 16 (2003) 895.
17 S. Y. Lee and B. Oh, J. Supercond., 16 (2003) 823.
18 J. Maziarska and C. Wilker, IEEE Trans. Appl. Supercond., 11 (2001) 4140.
19 P. Staszczuk, G. W. Chądzyński and D. Sternik, J. Therm. Anal. Cal., 62 (2000) 451.
20 G. W. Chądzyński, J. Therm. Anal. Cal., 71 (2003) 113.
21 K. Conder, E. Kaldis, M. Maciejewski, K. A. Müller and E. F. Steigemeier, Physica C, 210 (1993) 282.
22 G. W. Chądzyński, V. V. Kutarov and P. Staszczuk, J. Therm. Anal. Cal., 76 (2004) 633.
23 G. W. Chądzyński, J. Therm. Anal. Cal., 55 (1999) 661.
24 F. Paulik, Special Trends in Thermal Analysis, Wiley, Chichester 1995.
25 P. Staszczuk, D. Sternik, G. W. Chądzyński and V. V. Kutarov, J. Alloy. Compd., 367 (2004) 277.
26 S. Brunauer, P. H. Emmett and E. Teller, J. Am. Chem. Soc., 60 (1938) 309.
27 E. P. Barrett, L. G. Joyner and P. P. Halenda, J. Am. Chem. Soc., 73 (1951) 373.
28 B. M. Kats and V. V. Kutarov, Langmuir, 12 (1996) 2762.
29 A. B. Kisielev, The Structure and Properties of Porous Materials, Butterworths, London 1958, p. 195.
30 A. V. Neimark, Zh. Fiz. Khim., 64 (1990) 2593.
31 P. Pfeifer and D. Avnir, J. Chem. Phys., 79 (1983) 4573.
32 P. Pfeifer, Fractals in Physics, North-Holland, Amsterdam 1986, p. 72.
33 H. Shaked, P. M. Keane, J. C. Rodriguez, F. F. Owen, R. L. Hitterman and J. D. Jorgensen (Eds), Crystal Structures of the High-$T_c$ Superconducting Copper-Oxides, Elsevier, Amsterdam 1994.
34 K. Conder and Ch. Krüger, Physica C, 269 (1996) 92.