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## The Effect of Ageing on $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ Obtained by the Photoacoustic Method

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**Abstract:** Thermal diffusivity and electric transport properties of fourteen years old superconducting  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  pellets were obtained using the photoacoustic transmission technique and then compared with freshly made superconducting samples. The theoretical model for photoacoustic (PA) detection configuration is given. The measured amplitude and phase PA signals, as a function of the modulation frequency, were numerically analyzed. The thermal diffusivity, the coefficient of the carrier diffusion, optical absorption coefficient and the excess carrier lifetime were calculated. The thermal diffusivity of freshly produced samples decreased, after ageing, from about  $1.3 \cdot 10^{-6}$  to about  $6.1 \cdot 10^{-7} \text{ m}^2/\text{s}$ .

**Keywords:** Superconductor; Ageing;  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ .

**Резюме:** При помощи фотоакустического трансмиссионного метода определяли температуропроводность и транспортные свойства сверхпроводящих образцов  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  полученных синтезом 14 лет тому назад. Проведено сравнение полученных данных с результатами, полученными для свежесинтезированных образцов. Представлена теоретическая модель для фотоакустической трансмиссионной детектирующей конфигурации. Проведен цифровой анализ измеренных в функции частоты модуляции возбуждающего оптического пучка амплитудных и фазовых спектров. Рассчитаны температуропроводность, коэффициент носителей диффузии, коэффициент оптической абсорбции и продолжительность генерированных носителей. При старении температуропроводность сверхпроводящих образцов  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  снижается с  $1,3 \cdot 10^{-6}$  на  $6,1 \cdot 10^{-7} \text{ m}^2/\text{s}$ .

**Ключевые слова:** Сверхпроводник; старение;  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ .

**Садржај:** Применом фотоакустичне трансмисионе методе одређивани су топлотна дифузивност и транспортна својства суперпроводних узорака  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  који су синтезовани пре 14 година. Добијени резултати упоређивани су са резултатима добијеним за свеже синтезоване суперпроводне узорке. Дат је теоријски модел за фотоакустичну трансмисиону детекциону конфигурацију. Измерени фотоакустични амплитудски и фазни спектри у функцији учестаности модулације побудног оптичког снопа, анализирани су нумерички. Израчунати су топлотна дифузивност, коефицијент дифузије слободних носилаца, коефицијент оптичке апсорпције и време живота

генерисаних носилаца. Са старењем, топлотна дифузивност суперпроводних узорака  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  смањује се од  $1,3 \cdot 10^{-6}$  на  $6,1 \cdot 10^{-7} \text{ m}^2/\text{s}$ .

**Кључне речи:** Суперпроводник; старење;  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ .

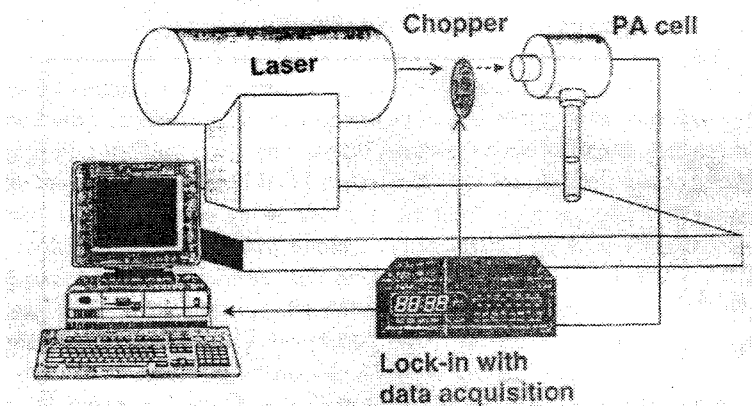
## Introduction

After Bednarz and Muller [1] discovered superconductivity at over 30 K in early 1986. in the class of ceramic oxides, which contain lanthanum, barium and copper, this new scientific field has been greatly developed. Various methods have been used for getting information in search for discovering the mechanism of superconductivity in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  and similar superconducting ceramics [2-4]. Some authors used even the photoacoustic and photothermal technique [5-7]. Kamimura and Sano [8] made cluster calculations, which were then used by Nawaura and Kamimura to calculate the many electron energy bands [9], the Fermi surfaces and the density of state for  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ . In this work we present the change of the thermal diffusivity and some electric transport properties of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  with ageing during a period of fourteen years.

## Experimental

Polycrystalline  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  samples were synthesized with a two-step method [4]. The superconducting powder was synthesized from powders of:  $\text{Y}_2\text{O}_3$ ,  $\text{BaCO}_3$  and  $\text{Cu}_2\text{O}$ , which were ground together using a vibration mill. The grain size of the powder was finally less than 2  $\mu\text{m}$ . The powder was annealed in an oxygen atmosphere at a pressure just over 1 atm. The temperature was slowly increased at the rate 1.5°C/min up to 950°C, and then kept at that temperature for about 6 hours. The obtained black powder was always superconducting. The superconducting powder then was pressed and sintered in the shape of pellets suitable for photoacoustic measurements. They were of a disk shape with a diameter of 10 mm. X-ray work was done before any other measurements and showed that both, fourteen years old and freshly made samples, had the same lattice structure.

The photoacoustic (PA) measurements were carried out using the experimental setup with a He-Cd laser (25 mW,  $h\nu = 2.8 \text{ eV}$ ) as an optical source given in Figure 1 where the laser beam was modulated with a mechanical chopper.



**Fig. 1** Experimental setup for PA measurements.

The PA cell was made in our laboratory [10] with a transmission detection configuration, given in Figure 2. The sample was mounted directly on the front side of an electret microphone where it should cover a 2.5 mm diameter circular window used for the sound inlet.

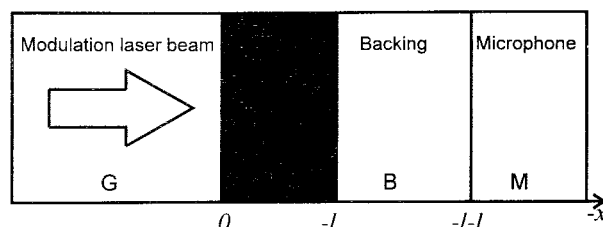


Fig. 2 The gas-backing-microphone-detection configuration.

## Results and Discussion

In Figure 3a, the diagrams of the PA phase spectra versus the modulation frequency were given for fourteen years old two  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  samples 610  $\mu\text{m}$  and 335  $\mu\text{m}$  thick with open circles and for a freshly made  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  sample 430  $\mu\text{m}$  thick with black squares. In Figure 3b the diagrams of the PA amplitudes for the same samples are given versus the modulation frequency. The old sample 610  $\mu\text{m}$  thick was polished with an abrasive silicon carbide P1000 sand paper and its thickness was decreased to 335  $\mu\text{m}$ . The freshly made sample was polished using the same procedure.

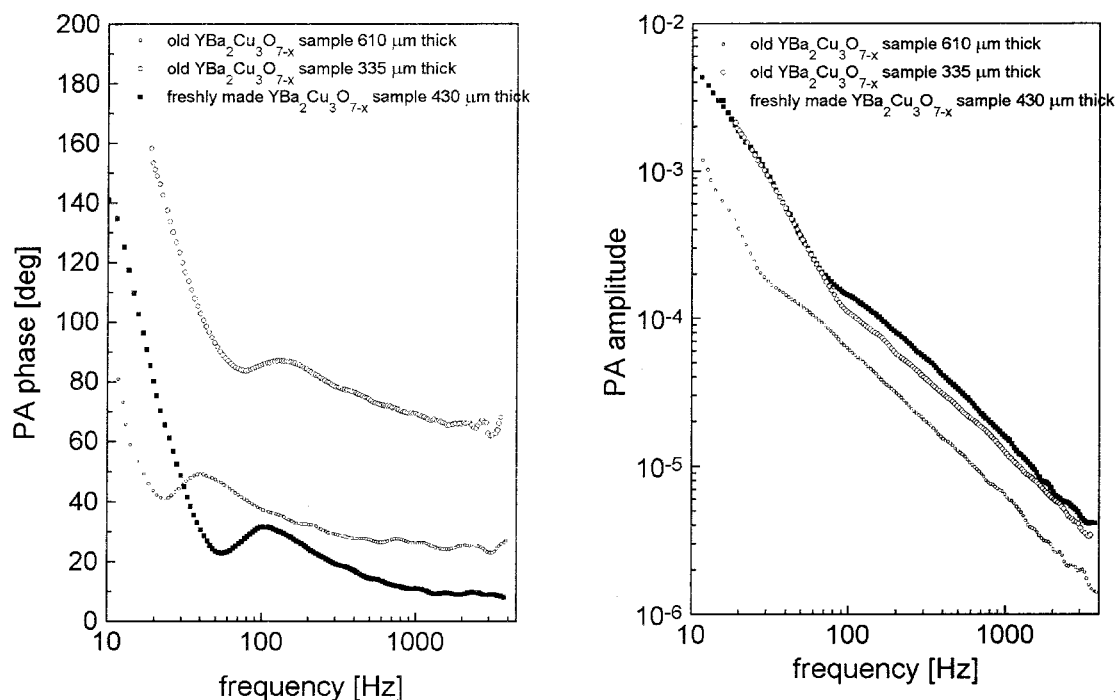


Fig. 3 The phase (a) and amplitude (b) spectra of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  old [14S (335  $\mu\text{m}$  thick) and 28S (610  $\mu\text{m}$  thick)] and freshly made [21S (430  $\mu\text{m}$  thick)] samples.

Theoretical analyses of the experimental results can be performed using the Rosencwaig-Gersho thermal piston model [11] where a gas-sample-backing-microphone configuration given in Figure 2 is considered. This theoretical treatment gives quantitative

account for the amplitude and phase of the PA signal describing also their dependence on the modulation frequency. Transmission detection configuration, in accordance with the Rosencwaig-Gersho theory, was then done by Pessoa et al. [12]. Then the PA signal can be expressed with the following relation:

$$S(-l, \omega) = \frac{\gamma P_0}{T_0 k_b l_b} \Phi_S(-l, \omega), \quad (1)$$

where  $l$  is the sample thickness,  $\omega$  is the frequency modulation of the excitation laser beam;  $\gamma$  is the adiabatic constant, while  $P_0$  and  $T_0$  are the ambient pressure and temperature, respectively.  $k_b = (1+j)/\mu_b$ , where  $\mu_b$  is the thermal diffusion length;  $l_b$  is the distance between the sample and microphone membrane and  $\Phi_S(-l, \omega)$  is the temperature variation of the sample surface which is in contact with the electret microphone.

The thermal diffusion length,  $\mu_b$ , can be expressed with the following equation:

$$\mu_b = \sqrt{\frac{2D_T}{\omega}}, \quad (2)$$

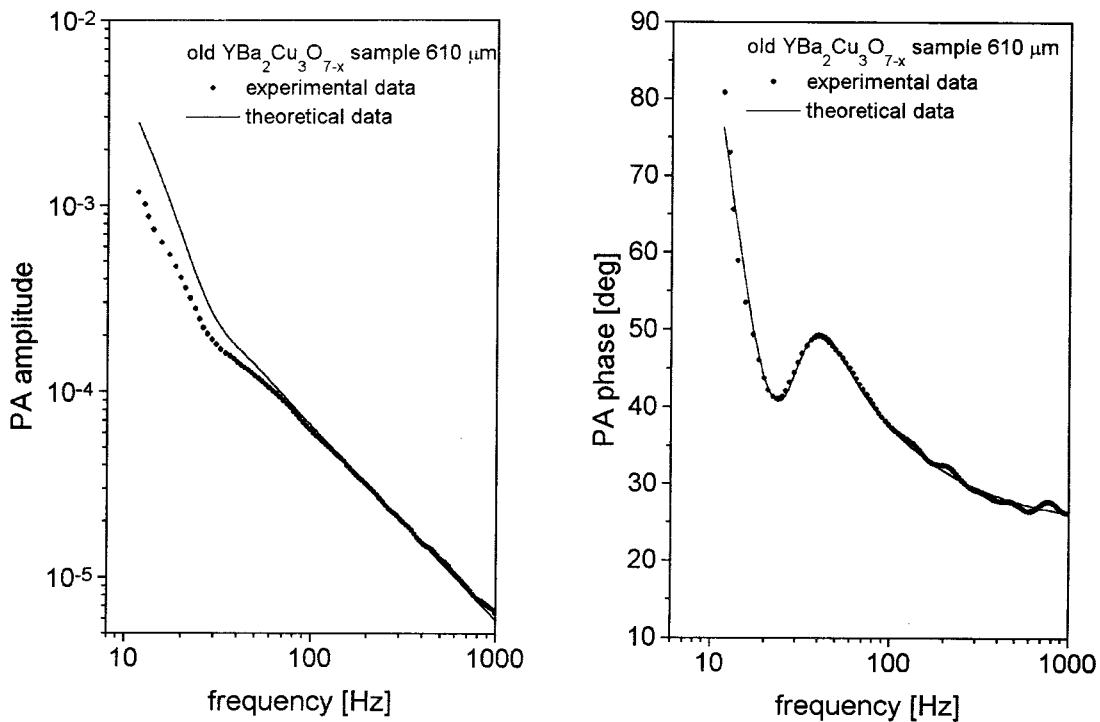
where  $D_T$  is the thermal diffusivity, which is the ratio of the thermal conductivity ( $K$ ) and the thermal capacity ( $\rho C_v$ )

$$D_T = \frac{K}{\rho C_v}, \quad (3)$$

where  $\rho$  is the density and  $C_v$  is the specific heat. A system of two coupled diffusion equations should be solved in order to determine the temperature variation, then, the density distribution of excess carriers and, finally, the amplitude and phase of the PA signal [13]. The theory predicts three general regimes. At low frequency the thermalization component is dominant, where the sample is thermally thin. The second regime is determined by excess carrier diffusion and recombination process, which is clearly seen at high modulation frequencies. The third regime is a complex interaction sensitive to excess carrier lifetime and surface recombination. It has intermediate frequencies.

The experimental results, phase and amplitude diagrams, were fitted with the theoretical curves obtained using the mathematical model for the given parameters and their values were determined during the fitting procedure. A fitting program was developed which enables the user to choose the values of parameters. It is possible to fit simultaneously the amplitude or the phase diagram or both together. There are also four criteria to estimate the fitting error. Mainly the sum of square of differences between the calculated and experimental values was used. A typical example of this fitting procedure of the phase and amplitude diagrams is shown in Figs. 4a, b for an  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  fourteen years old sample 610  $\mu\text{m}$  thick. The full line represents the theoretical curve while the experimental values are given with open circles.

In Table 1 the values of all previously mentioned adjustable parameters are given: thermal diffusivity ( $D_T$ ), excess carrier lifetime ( $\tau$ ), optical absorption coefficient ( $\alpha$ ), front ( $S_g$ ) and rear ( $S_b$ ) surface recombination velocity and the carrier diffusion coefficient ( $D$ ). Thermal conductivity was fixed. The literature value of  $K = 1 \text{ W/mK}$  given by Dyer et al. [14] was used.



**Fig. 4** The fitted PA phase (a) and amplitude (b) spectra of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> 14 years old sample versus the modulation frequency.

**Table 1** The values of thermal and electronic transport parameters for fourteen years old and freshly made YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> samples

Sample	Thickness (μm)	$D_T$ (m <sup>2</sup> /s)	$\tau$ (μs)	$\alpha$ (m <sup>-1</sup> )	$S_g$ (m/s)	$S_b$ (m/s)	$D$ (m <sup>2</sup> /s)
14S (old)	610	$0.61 \cdot 10^{-6}$	5.8	9128	211.8	9.7	$0.105 \cdot 10^{-3}$
28S (old)	335	$0.61 \cdot 10^{-6}$	3.8	16876	2444	4.04	$0.50 \cdot 10^{-4}$
21S (new)	430	$0.142 \cdot 10^{-5}$	4.9	12109	5784	0.02	$0.88 \cdot 10^{-4}$

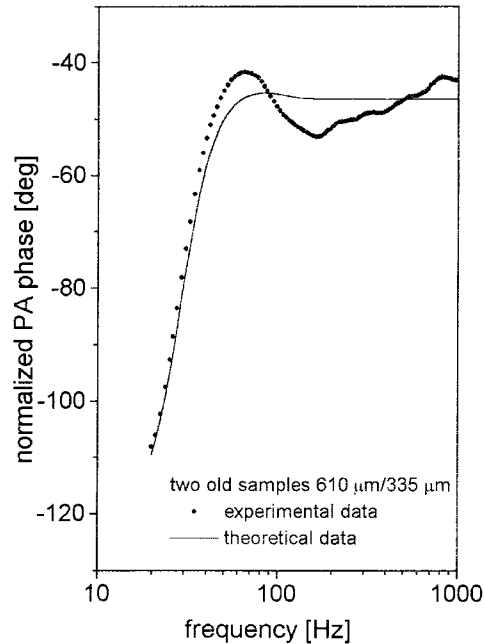
Looking at both phase and amplitude diagrams it is obvious that at low frequencies, where the electret microphone sensitivity decreases, some corrections could be done. One of the simplest methods for normalization of the PA signal is to take the signal ratio for two different thicknesses of the same sample whose thickness can be decreased by a polishing procedure.

The signal ratio can be calculated using the following equation obtained from equation 1:

$$\frac{S_1(\omega)}{S_2(\omega)} = \frac{\Phi(-l_1)}{\Phi(-l_2)} e^{j[\varphi_2(-l_2) - \varphi(-l_1)]} = A_n e^{j\Delta\varphi}, \quad (4)$$

where  $A_n$  is the amplitude ratio and  $\Delta\varphi$  is the phase difference of the experimentally measured PA signals for two different sample thicknesses.

In Figure 5 the PA phase difference normalized fitted diagrams for two samples of fourteen years old  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  samples ( $610 \mu\text{m} / 335 \mu\text{m}$  is the ratio of thickness) is given. The obtained value of thermal diffusivity is the same like the one in Table 1 and the values of the other parameters are very similar so they need not be given. It is interesting to notice that the thermal diffusivity for fourteen years old sample is reduced compared with the freshly made sample for about 2.3 times. The reason for this decrease of the thermal diffusivity with ageing of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  for the old sample is that the content of oxygen decreases with ageing. For the freshly made sample the content of oxygen is 6.9 [15] and it decreases to 6.55 for fourteen years old samples.



**Fig. 5** The corrected and fitted PA sample 14 years old  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  sample [28S (335  $\mu\text{m}$  thick)] versus modulation frequency.

## Conclusion

Fourteen years old superconducting  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  samples were examined using the photoacoustic method with a transmission detection configuration. The obtained results were compared with a freshly made sample. By comparing experimental results and theoretical curve using a parameter fitting method it was determined that the thermal diffusivity decreases from about  $0.142 \cdot 10^{-5}$  to about  $0.61 \cdot 10^{-6} \text{ m}^2/\text{s}$  after fourteen years. This is in agreement with the decrease of the oxygen content for the new (6.9 per one atom of yttrium) and aged sample (6.55 per one atom of yttrium). Besides thermal diffusivity we calculated some other electronic transport properties and optical absorption coefficient for new and old samples. The hole diffusion coefficient slightly decreased also with ageing while the excess carrier lifetime remains several microseconds and the optical absorption coefficient does not change very much. In our previous work we found that in the old sample the superconducting properties decreased to about one third of its superconducting phase. The results obtained in this work are in reasonable agreement with this because the thermal diffusivity decreases for about 2.3 times with ageing.

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