Distance to Massive Metal Body—a Paradoxical Parameter that Regulates the Intensity of the Hydration of YBa$_2$Cu$_3$O$_{6.75}$

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Abstract

The effect on the hydration of YBa$_2$Cu$_3$O$_{6.75}$ (YBCO) of a closely placed non-magnetic and non-charged steel disk is examined. For this purpose, it is utilized a previously developed special method of material preparation that has been published earlier. The resulting material is analyzed by the iodometric titration technique, X-ray diffraction, and X-ray photoelectron spectroscopy. Conducting the experiment on the YBCO samples being hydrated at different distances from the steel disk clearly indicates a significant inhibitory effect of this factor. We find that there is a certain distance from the surface of the metal body, at which the hydration process achieves maximum sensitivity to the metal presence. At this stage of research, it is assumed that the mediator, with the aid of which the influence on the hydration process occurs, might be electromagnetic radiation emanating from an YBCO sample and reflected from the surface of metal.

Keywords: YBa$_2$Cu$_3$O$_{6+\delta}$ · X-ray photoelectron spectroscopy · Hydration · Inhibitory effect

1 Introduction

A fairly limited number of chemical processes are known that can be influenced by external fields. The category of processes affected by magnetic field includes [1–3] recombination of radicals, processes in biological systems, some adsorption processes. But only some biological systems and biochemical processes going in them are affected by electric and electromagnetic fields [4]. All the systems that can be influenced by external fields are in critical state relative to their instability. At the same time, the detailed mechanism of the action of external fields on them is still not entirely clear [1–4]. In most cases, however, chemical processes do not react to either magnetic or electric field. Along with this, there are no any mentions in literature about the impact on chemical processes of non-magnetic and non-charged bodies which do not have direct contact with the reagents.

In our previous work [5], we studied the hydration of YBa$_2$Cu$_3$O$_{6.75}$ (YBCO) which is a superconductor with a critical temperature of about 70 K. This compound is chemically active with respect to water and as a result of prolonged contact with the moist environment that can chemically degrade, losing its practical performance properties [6, 7]. In [5], however, we used a previously developed method of material preparation, such one that enables hydration process in the final product to proceed at relatively low humidity, $P_{H_2O} = 0.9–1.0$ kPa. 1

Hydration process carried out in such way does not lead to a sensitive chemical degradation of the material even at a high degree of saturation of it with water. 2 The most surprising thing we revealed in [5] was that the hydration kinetics of YBCO was significantly influenced by the close location of the neighboring YBCO samples to each other. Meanwhile, the samples manifested very weak magnetic properties, and external fields: magnetic and electric did not affect the hydration process in them up to high values of field strength. An attempt to shield one of the interacting samples with an aluminum foil jacket did not affect the result of their interaction. In addition, signs of the influence on YBCO of other massive bodies, which are not superconductors, were found. Thus, upon the results of the work [5], two main unresolved questions have been remaining: what is the nature of

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1 The other methods of material preparation give the product that is chemically stable in the humidity range of 0.9–1.0 kPa (see, for example, [8, 9]). Usually, in practice, the superconductors work namely in this range of $P_{H_2O}$.

2 It is possible that there is also the saturation of YBCO with oxygen here [5], but this point needs to be proven in additional experiments.

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the impact of YBCO samples on each other while they are being hydrated? And whether other bodies located next to YBCO samples can indeed influence the hydration process in them?

In the present paper, we conduct a study on how a massive steel disk located in the close vicinity of YBCO affects the hydration process proceeding in this oxide at low $p_{H_2O}$. Conducting this experiment on the YBCO samples being hydrated at different distances from the disk clearly indicates a significant inhibitory effect of this factor.

2 Experimental Details

The YBCO material for this study was prepared by the sintering method from oxides of yttrium and copper and barium carbonate. The powders were mixed in stoichiometric proportions and heat treated first at 750 °C for 5 h, then at 940 °C for 150 h with intermediate grindings. After that, the product was saturated with oxygen at 585 °C for 5 h in flowing air. The resulting material was examined by the iodometric titration technique for the oxygen content value. The powders were mixed in stoichiometric proportions and heat treated first at 750 °C for 5 h, then at 940 °C for 150 h with intermediate grindings. After that, the product was saturated with oxygen at 585 °C for 5 h in flowing air. The resulting material was examined by the iodometric titration technique for the oxygen content value.

The YBCO samples were placed on a steel disk located in the close vicinity of YBCO affects the hydration process proceeding in this oxide at low $p_{H_2O}$. Conducting this experiment on the YBCO samples being hydrated at different distances from the disk clearly indicates a significant inhibitory effect of this factor.

3 Experimental Results

3.1 The Hydration Kinetics of YBCO

Figure 2 shows examples of the hydration kinetics of the dispersed YBCO samples which are assumed to be not influenced by any surrounded bodies. On the basis of a plenty of kinetic curves obtained by us, it can be stated that the hydration process under investigation proceeds equally for all samples (of type I and II), and it is characterized by reproducibility. Hydration process proceeding under the influence of steel disk will be further characterized with a parameter “relative hydration rate” of the lines was $Δ2θ = 0.015°$.

The X-ray photoelectron spectroscopy (XPS) study was carried out on an electron spectrometer Multiprobe Compact equipped with an energy analyzer EA-125 (Omicron, Germany). An X-ray tube with magnesium anode of 180 W was used as the X-ray source. The spectral data acquisition was made with a step of 0.1 eV, an acquisition time of 7.5 s per step, and a passing energy of 20 eV. The element concentrations were calculated according to Eq. 1:

$$X_i = \frac{I_i \sigma_i \phi(E_h)}{\sum_i I_i \sigma_i \phi(E_h)},$$

where $X_i$ is the $i$th element fraction in the surface layer studied; $\sigma_i$ is the photoionization cross-section for the $i$th element [10]; $\phi(E_h)$ is a factor depending on the binding energy, which is determined while calibrating the spectrometer using standard samples. It is considered that if these standards are used then XPS quantitative measurements are as accurate as $±5%$. The depth of the XPS analysis is considered to be 5–10 nm.
(RHR), which will allow comparing numerically its kinetics for various YBCO samples:

\[ \text{RHR} = \left( \frac{\alpha}{\alpha_{\text{max}}} \right) \times 100\% \]

where \( \alpha \) and \( \alpha_{\text{max}} \) are the degrees of moisture-saturation for 4 days of the samples that are subject and not subject to the influence of steel disk, respectively.

### 3.2 Characterization of the Initial and Hydrated YBCO by XRD and XPS

The structural data and phase composition of the YBCO material at different stages of its treatment are presented in Table 1. One can state that the YBCO phase is rather contracted after exposure to humid air. The lattice parameters of exposed YBCO correspond to the maximally oxidized state of YBCO [11]. On the other hand, our study has not revealed radical changes in the structure that would be evidence of the transformation of YBCO under the action of absorbed water into the pseudo-\( \text{YBa}_2\text{Cu}_4\text{O}_8 \) phase, as had been observed in [12], or into another phase. There is observed only some change in the phase composition caused by the deposition of the impurity phases.

Results of the XPS measurements on the samples before and after exposure to humid air are depicted in Fig. 3. XPS survey spectra (Fig. 3a) show signals of all characteristic electronic levels of the elements that constitute the samples under study. A quantitative assessment of the ratio between these elements, performed according to Eq. 1, is presented in Table 2.

In [13], the \( \text{RBa}_2\text{Cu}_3\text{O}_{6+\delta} \) (\( R = \text{Y}, \text{Nd} \)) oxides have been studied by XPS, and a detailed analysis of high-resolution XPS spectra concerning these compounds has been performed. According to this work, it is convenient to evaluate the phase composition of the YBCO surface layer when considering the Ba 3d spectra (which are 3d_{3/2}–3d_{1/2} doublets due to spin-orbital splitting), since this electronic level is characterized by large chemical shifts. High-resolution spectra of copper and yttrium are less informative from this point of view. In [13], the Ba 3d–binding energy in various phases containing Y, Ba, and Cu has been determined. Based on these data, to peaks at 777.6, 779.8, and 781.7 eV in the Ba 3d

| Table 1 | The structural data and phase composition of the YBCO samples before and after exposure to humid air |
|-----------------------------------------|-----------------------------------------|
| Structural parameter | Before exposure to humid air | After exposure to humid air |
|-----------------------|-----------------------------|-----------------------------|
| Major phase, space group (Pmmn) | | |
| \( a \) (Å) | 3.8284 (1) | 3.8270 (1) |
| \( b \) (Å) | 3.8884 (2) | 3.8833 (1) |
| \( c \) (Å) | 11.7063 (5) | 11.6931 (3) |
| \( V \) (Å) | 174.264 (7) | 173.776 (6) |
| Impurities | \( \text{Y}_2\text{BaCuO}_5 \) (~3%) | \( \text{Y}_2\text{BaCuO}_5 \) (~3%) |
| | \( \text{Ba}_2\text{Cu}_3\text{O}_{6.9} \) (~2%) | \( \text{BaCuO}_{2.36} \) (~2%) |

![Graph](image_url)

**Fig. 2** The hydration kinetics of the YBCO samples at a humidity of 43% and a temperature of 24 °C. It is shown the method of determination of the parameter \( \alpha_{\text{max}} \)
spectra obtained by us (see Fig. 3b), we put into correspon-
dence the phases YBCO, BaCO₃, and Y₂BaCuO₅/BaₓCuₒₓ₋ₓ
(y the Ba 3d–binding energies in the Y₂BaCuO₅ and
BaₓCuₒₓ₋ₓ phases are about the same).

Analyzing the data shown in Fig. 3 and Table 2, we can
conclude that during the hydration process the material sur-
face layer becomes depleted in yttrium atoms and enriched in
copper. Shares of barium and oxygen vary slightly. Such
changes can only be explained by the appearance in the chem-
ical system of a large volume of copper-containing phases,
which do not contain yttrium, i.e., BaₓCuₒₓ₋ₓ. The relative
volume of these phases must be large enough to compensate
in excess for the disappearance of the main phase in the hy-
drated sample (this disappearance has arisen because of the
impurity layer thickness exceeded up the thickness of the layer
analyzed by XPS 5–10 nm). This is completely consistent
with the XRD data (see Table 1) according to which about
4 vol.% of BaₓCuₒₓ₋ₓ emerges in YBCO in the course of its
hydration.

It should be noted that the formation of the BaₓCuₒₓ₋ₓ phases is not the characteristic of the hydration of YBCO,
but is the characteristic of that for NdBa₂Cu₃O₆₊₅ (NBCO)
[13]. As suggested in [13], this difference is associated with
faster water molecule diffusion in the NBCO structure com-
pared with their diffusion in YBCO. We believe that the ap-
pearance in the present study of the BaₓCuₒₓ₋ₓ phases as the
hydrolysis product is precisely due to the high-diffusion rate
of H₂O (see Fig. 2) in the YBCO material prepared according
to the new method (see paragraph 2).

### 3.3 The Effect of a Massive Steel Disk on the Hydration Kinetics of YBCO

Figures 4 and 5 show the complete array of experimental data
on the effect of the massive steel disk on the hydration of
YBCO, accumulated for a long period of time and represented
here in the form of RHR(W) dependences. An interesting
feature of the hydration process, which has been already noted
by us in the previous work [5], is striking—for a small sample
weight (less than a certain value of Wₘₐₓ), the process is prac-
tically not implemented. As seen from Figs. 4 and 5, the

| Table 2 The elemental composition of the YBCO sample surface layer before and after exposure to humid air |
|-------------------------------|-------------------|
| Element | Before exposure to humid air | After exposure to humid air |
| Y | 0.196 | 0.042 |
| Ba | 0.115 | 0.081 |
| Cu | 0.122 | 0.188 |
| O | 0.567 | 0.689 |

Fig. 4 Dependences of the relative rate of the hydration of YBCO (relative to the maximum rate for a given batch of samples) on the weight of the sample of type I
values of the parameter $W_{\text{thr}}$ for samples with diameters 3.0 and 7.3 mm are $63 \pm 4$ and $305 \pm 5$ mg, respectively. Taking into account the convex bottom of the samples of small diameter, which should lead to somewhat overestimated values of $W_{\text{thr}}$, one can consider that $W_{\text{thr}} \propto d^2$, where $d$ is the sample diameter. In other words, the critical value of $W$ is proportional to the area of the sample base. Therefore, the value of $W_{\text{thr}}$ is achieved for all samples with a certain height $h_{\text{thr}}$. For the dispersed YBCO material used in our work, which has the bulk density $\rho = 3.7$ mg·mm$^{-3}$, it is easy to obtain from the equation

$$h = 4W/\rho \pi d^2$$  

(3)

that $h_{\text{thr}} = 2.1 \pm 0.2$ mm (as a control, in Figs. 4, 5, 6, and 7, the auxiliary horizontal axis $h$ is shown, the values on which are set based on Eq. (3)). This result matches the direct measurements $h_{\text{thr}}$, which we were carrying out during the research. One, however, refutes the assumption we made earlier [5] that $h_{\text{thr}}$ depends on $d$. The critical value of $W$ does not seem to depend on the presence of the massive steel disk near the samples. At the same time, the influence of the disk on the behavior of the RHR($W$) dependences is quite noticeable at $W > W_{\text{thr}}$.

As it follows from Figs. 4 and 5, when the steel disk is located far from a sample ($l = 25$ mm), then the increase in the hydration intensity at $W = W_{\text{thr}}$ occurs abruptly to maximum value. Then, at $W > W_{\text{thr}}$, the hydration kinetics remains at the highest level regardless of $W$, which is true for any type of samples. We will consider such behavior as free from the influence of metallic body. As the steel disk approaches the sample, its inhibitory effect on the hydration kinetics of YBCO first increases, and then, after passing through a maximum at $l_{\text{max}} = 5 \div 6$ mm, it begins to decrease. In this case, the steel-disk-effect itself is manifested differently for various values of $l$. For $l \leq l_{\text{max}}$, it is characteristic that the RHR($W$) dependence sharply increases at $W_{\text{thr}}$, after which gradually decreases. For $l \geq l_{\text{max}}$, the delayed hydration kinetics is revealed already at $W_{\text{thr}}$.

### 4 Discussion

The results obtained unambiguously indicate the existence of some influence from the side of the steel disk on the hydration of YBCO. Moreover, this impact is extreme, depending on the distance to the disk. As for the difference in the shape of the RHR($W$) dependences for cases $l \leq l_{\text{max}}$ and $l \geq l_{\text{max}}$, it should be kept in mind that various parts of the sample are located at different distances from the disk, experiencing, therefore, non-equal intensity of its effect. With the sample weight increasing, this difference should manifest itself more and more significantly and differently, depending on where the sample is located relative to $l_{\text{max}}$. In order to visually illustrate how the shape of the RHR($W$) dependences can change with changing $l$ parameter, we will try to simulate the effect of the disk on the hydration of YBCO. For this purpose, the parameter $Q$ denoting intensity of the impact of the steel disk on a unit volume of YBCO is introduced. We assume in the first approximation that at a unit exposure of this kind $5$ (i.e., when $Q = 1$ arbitrary units), for an YBCO unit volume under consideration, the relative hydration rate (RHR) decreases by $x\%$. Thus it turns out that $\text{RHR} = 100 - x \cdot Q$. As a functional dependence of the intensity $Q$ on the distance $r$ between the

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4 Due to the corresponding features of the bottom of tubes in which these samples were located.

5 Here we do not take into account the nature of this impact. We only consider its inhibitory effect on the hydration of YBCO.
disk and the sample unit volume under consideration, it is convenient to choose the following:

\[ Q(r) = \frac{1}{ar^2 - 2ar_{\text{max}}r + c}, \quad (4) \]

as the most suitable for describing our experimental results, where \( r_{\text{max}} \) is the distance to the disk at which the function \( Q(r) \) shows a maximum. The values of coefficients \( a \) and \( c \) are 125 and 4501 for samples of type I, and are 33 and 2129 for samples of type II. The values of the parameter \( r_{\text{max}} \) are 6 and 8 for the samples of type I and II, respectively. Then the relative rate of hydration is described by the equation:

\[ \text{RHR} = 100 - \frac{x}{h} \int_0^{l+h} \frac{dr}{ar^2 - 2ar_{\text{max}}r + c}, \quad (5) \]

in which the height of the sample \( h \) can be calculated from Eq. (3). The \( Q(r) \) dependence is shown in Figs. 6a and 7a, and the simulated RHR(W) curves calculated on its basis with using the value of the parameter \( x = 2000\% \), in Figs. 6b and 7b. It can be seen that the calculated dependences are in satisfactory agreement with the experimental ones obtained for various values of \( l \), but only in the final part of them. In their initial part, the experimental dependences are not described by the given calculated. However, here we are dealing with a still unexplored effect of a sharp increase in RHR at \( W_{\text{thr}} \), which cannot be considered in the framework of this simple model.

The above comparison clearly demonstrates that the effect of the massive steel disk on the hydration of YBCO found in our experiments does not have a random character. It can be described as the impact on YBCO of a certain potential \( Q \) having a sharp maximum on some distance from the disk. The current study has not revealed a cardinal difference in the effect of this potential on samples of type I and type II.

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**Fig. 6** a The intensity of impact of the steel disk on unit volume of the YBCO sample of type II depending on the distance to the steel disk surface. b Calculated dependences RHR(W), obtained with using Eq. (5) in comparison with experimental fitting lines in Fig. 5

**Fig. 7** a The intensity of impact of the steel disk on unit volume of the YBCO sample of type I depending on the distance to the steel disk surface. b Calculated dependences RHR(W), obtained with using Eq. (5) in comparison with experimental fitting lines in Fig. 4
generate a wave structure similar to that shown in Figs. 6a and 7a. The superposition of incident and reflected waves can, in principle, explain the observed bursts of the signal, similar to the result of wave interference. It is quite obvious that the steel disk itself cannot create any radiation (except for resonant acoustic). Meanwhile, it can serve as a reflector of electromagnetic radiation coming from YBCO. Free penetration of the radiation through the aluminum screen surrounding samples of type II supports this suggestion. The resulting superposition of incident and reflected waves can, in principle, generate a wave structure similar to that shown in Figs. 6a and 7a (this structure may actually be somewhat different, since we used a very simplified model to simulate it).

The small difference in the position of its maximum \( r_{\text{max}} \) observed for these two types of samples is associated, in our opinion, with a more than twofold difference in the diameter of the samples (we intend to further study in more detail the effect of various factors on \( r_{\text{max}} \)).

Depicted in Figs. 6a and 7a, \( r \)-dependences of \( Q \) are very similar to the result of wave interference. It is fairly obvious that steel disk itself cannot create any radiation (except for resonant acoustic). Meanwhile, it can serve as a reflector of electromagnetic radiation coming from YBCO. Free penetration of the radiation through the aluminum screen surrounding samples of type II supports this suggestion. The resulting superposition of incident and reflected waves can, in principle, generate a wave structure similar to that shown in Figs. 6a and 7a (this structure may actually be somewhat different, since we used a very simplified model to simulate it).

To date, it has not been recorded any continuous radiation coming from an YBCO-sample either during or after its hydration. However, when studying magnetic properties of the hydrated YBCO samples using a vibration magnetometer (see [5]), we sometimes observed bursts of the signal, similar to those shown in Fig. 8. Moreover, as already reported in [5], after holding one of the hydrated samples in a dry atmosphere for 3 days, its temperature dependence of magnetic moment shows the dependence of magnetization of the YBCO sample which at the beginning was saturated with water and then was stored in a dry atmosphere for 3 days.

Along with this, it is still difficult to explain the sustain position of the maximums in the \( Q(r) \) dependences (see Figs. 6a and 7a), which are independent of the distance between disk and sample. Thus, the question regarding the nature of radiation emanating from the hydrated YBCO samples will remain without a final answer.

5 Conclusion

Studying of the hydration of YBCO has indicated that this process is subject to the inhibitory effect of an external factor that was previously considered as not significant—the presence of a massive metal body near the sample being processed. It has been found that there is a certain distance from the metal body surface, at which the sample is exposed to maximum effect. This distance relates with the diameter of the sample. At this stage of research, it is assumed that the mediator, with the help of which the influence on the hydration process occurs, might be electromagnetic radiation emanating from a neighboring sample or reflected from the surface of metal body.

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