

**THE OPTIMIZATION OF THE COMPOSITION,
STRUCTURE AND PROPERTIES OF METALS, OXIDES,
COMPOSITES, NANO- AND AMORPHOUS MATERIALS**

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The study of the electroconductivity of polycrystalline $\text{Na}_2\text{O}-n\text{Al}_2\text{O}_3$ samples ($5.5 \leq n \leq 9.5$) at 313-625K has been performed. It was shown that the specific resistance decreases with the increase in Na_2O content due to the increase in the content of β -alumina phase. The study of the sample with $\text{Na}_2\text{O}-6\text{Al}_2\text{O}_3$ composition indicated that the increase in the compacting pressure results in the decrease in the final ceramics conductivity.

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MAGNETIC PROPERTIES OF MECHANOACTIVATED OXIDE Mn_3O_4

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ABSTRACT

A magnetic study of the original coarse-grained and mechanically activated Mn_3O_4 powders is presented. It is shown that the mechanical activation of powder is confirmed by the significant decrease in the magnetization. The paramagnetic (PM) - ferrimagnetic (FiM) transition temperature is reduced also.

INTRODUCTION

Study of the different properties of mechanoactivated oxides makes it possible to determine the activation process influence on the structure, defectiveness, cation distribution, charge and orbital states of ions. As one of the consequences of the intensive mechanical activation is the appearance of nanodisperse states, specificity of considered properties in nanocrystalline oxides is considered at the same time. It is known now that the decrease in the crystallite size causes a decrease of some phase transition temperatures and such characteristics as latent heat and order parameters. The processes of mechanoactivation may also lead to new types of phase states due to the redistribution of cations between the crystallographically inequivalent sublattices of the crystals, redox reaction and other. In the present work the main attention is devoted to the analysis of the activation effects associated with the magnetic properties of Mn_3O_4 oxides in metastable state at low temperatures.

Sample preparation and characterizations

This paper studies the differences of magnetic properties of the original coarse-grained S_1 and mechanically activated S_2 samples of oxide Mn_3O_4 . Mechanoactivation was carried out in vario-planetary mill Pulverizette 4 (Fritsch) in glasses of tungsten carbide. Volume of drum was equal to 250ml, loading of crushing balls was 800g and a material mass was 20 g. Milling was made "dry", the duration was 3 min.

The phase composition of obtained substances, the size of coherent scattering domains (CSD) and microstresses were determined by X-ray diffractometer D8 ADVANCE (Bruker) (radiation $\text{CuK}\alpha$, Ni-filter, position-sensitive detector VANTEC1). High-temperature X-ray studies of the stability of mechanoactivated oxides was carried out using high-temperature chamber HTK1200N (Anton Paar).

The results of the diffraction analysis of the initial and mechanoactivated oxides Mn_3O_4 are presented in Table 1-2.

The presented data on the temperature behavior of the grinded for 3 minutes oxide Mn_3O_4 show that mechanoactivation treatment with a small amount of centrifugal factor (20g) and short times save the phase composition of the powder at temperatures below 30°C.

Table 1. Characteristics of initial and mechanically activated manganese oxides Mn_3O_4

Sample	Crystal phase	The average size of coherent scattering domains, nm	The crystal lattice parameters	
			a, Å	c, Å
S ₂	Mn_3O_4	12	5.766	9.464
S ₁	Mn_3O_4	>200	5.760	9.474

Table 2. The temperature boundaries (°C) of the phase existence during heating and cooling of mechanically activated manganese oxides Mn_3O_4

Sample	Crystal phase	Heating		Cooling	
		from	to	from	to
S ₂	Mn_2O_3	455	905	-	-
	Mn_3O_4 (hausmannite)	30	1160	1100	30
	Mn_3O_4 (spinel)	1120	1200	1200	1040
S ₁	Mn_2O_3	685	945	-	-
	Mn_3O_2 (hausmannite)	30	1160	1090	30
	Mn_3O_2 (spinel)	1125	1200	1200	1010

Magnetization measurements

The field-cooled (FC) and zero-field-cooled (ZFC) temperature dependences of magnetization and the hysteresis curves were performed with using of a vibrating sample magnetometer Cryogenic CFS-9T-CVII. In ZFC mode, the sample has been cooled from room temperature to 4 K in the absence of *dc*-magnetic field, then the field was applied at 4 K and magnetization data were recorded while increasing the temperature. In FC mode, the sample was cooled from room temperature to 4 K in presence of *dc*-magnetic field (same magnitude which was applied during ZFC measurement) and the magnetization data were recorded with increasing temperature. The temperature dependences of the *dc*-susceptibility for the samples S₁ and S₂ measured under ZFC and field-cooling FC conditions are presented in Fig. 1-4.

Before discussion of these results it is necessary to note that in the oxide Mn_3O_4 prepared by various methods ferrimagnetic ordering takes place at $T_c = 43$ K [1]. Besides the phase transitions attributed to the spin reorientations were observed at 39 and 32 K [1-3] in the single crystal Mn_3O_4 .

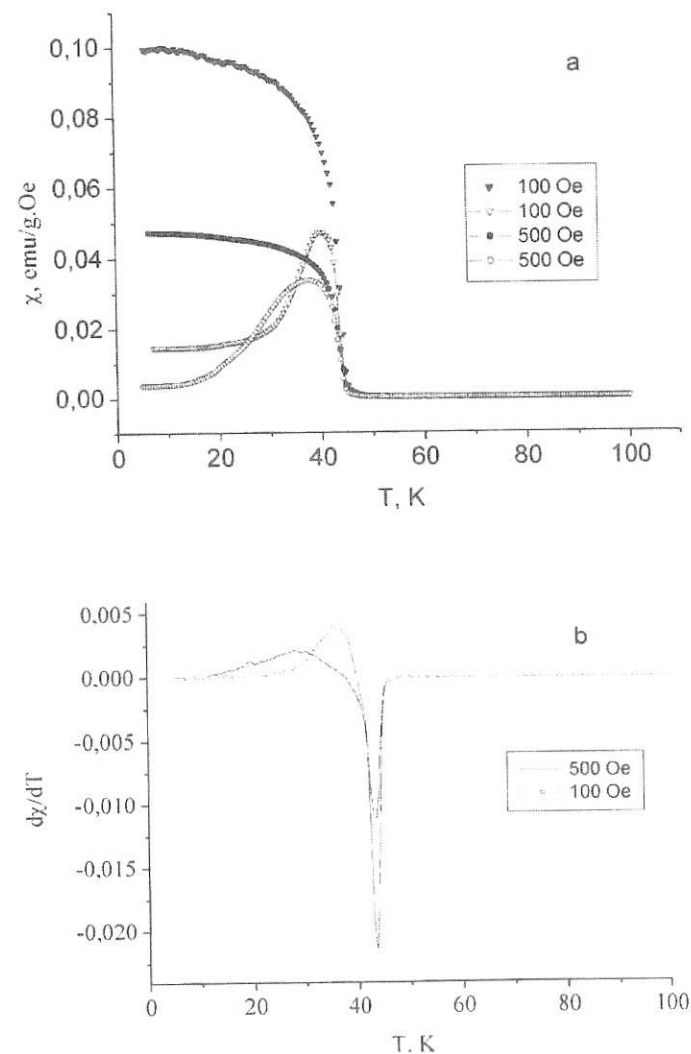


Fig. 1. FC and ZFC susceptibilities of Mn_3O_4 powder S₁ as a function of temperature recorded at two different applied fields (a) and the temperature derivative of the ZFC susceptibility (b).

Open symbols correspond to ZFC data while closed symbols indicate FC data.

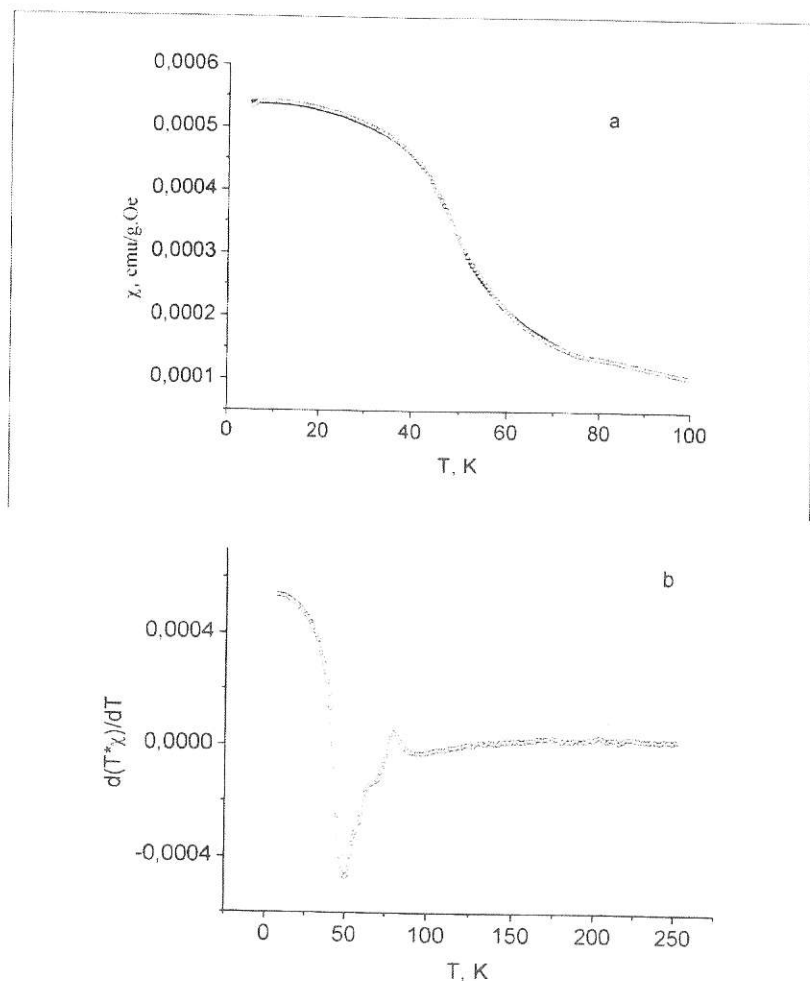


Fig. 2. FC and ZFC susceptibilities of Mn_3O_4 powder S_1 as a function of temperature recorded at applied field 80 kOe (a) and the temperature derivative of the function $\partial(T \cdot \chi)/\partial T$ (b) for ZFC case.

Open symbols correspond to ZFC data while closed symbols indicate FC data.

One can see (Fig. 1) that both ZFC and FC susceptibilities for the sample S_1 are almost independent of temperature above 50 K and near identical. The FC and ZFC curves start to separate below the irreversibility temperature $T_{irr} = 46$ K at weak magnetic fields (100 Oe and 500 Oe). The appearance of temperature magnetic

irreversibility (TMI) between the FC and ZFC branches indicates an induced preferential orientation of the particle moments along the applied field. The peaks in the ZFC curves are the blocking temperatures T_B : $T_B = 40$ K for 100 Oe and 38 K for 500 Oe.

It is known that both temperatures T_B and T_{irr} decrease with increase in applied field. In agreement with this we have observed the decreasing of T_B and T_{irr} with increasing of the applied field.

The ferrimagnetic transition temperature T_c for the samples Mn_3O_4 was determined by taking the derivative of the susceptibility against the temperature. The transition temperature does not change with the applied field 100 Oe and 1000 Oe. This is determined to be 43 K for the sample S_1 in good agreement with literature values of bulk Mn_3O_4 at 43 K [1-3]. The phase transitions at 39 and 32 K were not observed in our samples.

The mechanical activation of Mn_3O_4 powder was confirmed by the significant decrease in the magnetization of the sample S_2 at $T = 4$ K: $m_2 \approx 4.5$ emu/g compared with the corresponding value $m_1 \approx 10$ emu/g for the sample S_1 in the FC condition with the applied field 100 Oe. Difference in the magnetization for the samples S_1 and S_2 also stored in a strong magnetic field $H = 80$ kOe: $m_1 = 43.2$ emu/g, $m_2 = 32.3$ emu/g. The effect might be attributed to the increasing of surface to volume ratio, since the surface region leads to a decrease in the effective magnetic moment. The FC and ZFC curves for the sample S_2 start to separate at $T_{irr}(S_2)$, lying in the range $(80 \div 100)$ K for magnetic fields $(100 \div 1000)$ Oe, which is significantly higher than for initial sample S_1 . The increasing of the applied magnetic field leads to a decreasing of the blocking and irreversibility temperatures as in the case of the sample S_1 . The ferrimagnetic transition temperature T_c is equal to 41 K for the sample S_2 . The directed change of the magnetic properties of Mn_3O_4 powder can be attributed both due to size effects and the disproportional reactions, the redistribution of cations between the crystallographically inequivalent sublattices of the crystal, the vacancy formation at mechanoactivation.

For the both samples $T_c(Mn_3O_4)$ reaches a value $T_c = 48$ K in applied magnetic field 80 kOe. At the same time TMI completely disappears. Along with this, at higher temperature (~ 80 K) the new anomaly is evidenced. This anomaly is defined only in the case of strong magnetic field (80 kOe), as can be observed from the Fig. 3-4. It can be admitted that a second magnetic phase with a magnetic ordering temperature higher than $T_c(Mn_3O_4) = 43$ K is presented in the samples. A neutron study of the $\alpha - Mn_2O_3$ oxide has shown [4] that majority of the magnetic peaks disappear above $T_N \approx 80$ K. Therefore, the added extremum of the function [redacted] can be given a simple explanation by invoking of magnetic properties of Mn_3O_4 and $\alpha - Mn_2O_3$ phases. At that it is important to note that the existence of the $\alpha - Mn_2O_3$ phase is demonstrated most obviously in the case of mechanoactivated sample.

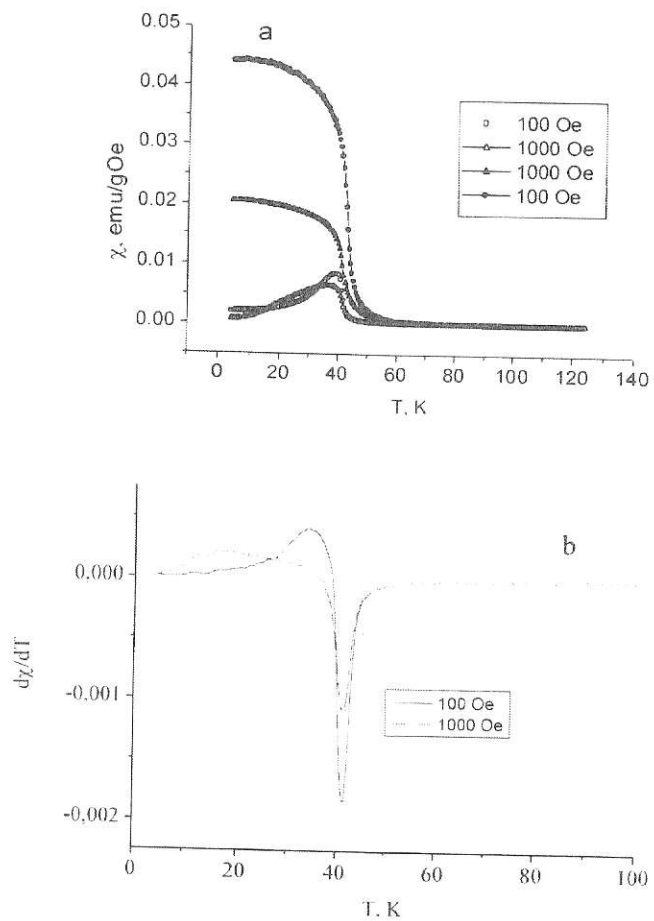


Fig. 3. FC and ZFC susceptibilities of Mn_3O_4 powder S_1 as a function of temperature recorded at two different applied fields (a) and the temperature derivative of the ZFC susceptibility (b).

Open symbols correspond to ZFC data while closed symbols indicate FC data.

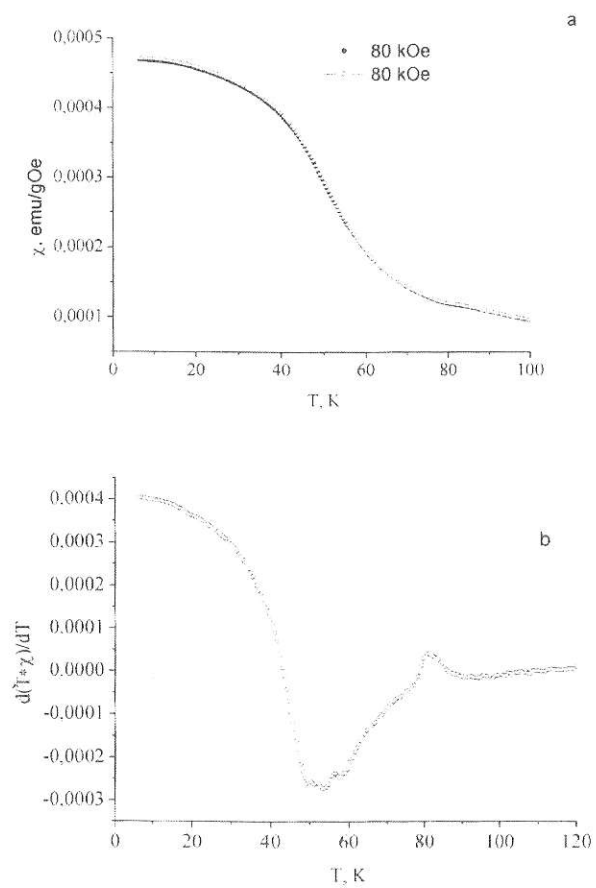


Fig. 4. FC and ZFC susceptibilities χ of Mn_3O_4 powder S_2 as a function of temperature recorded at applied field 80 kOe (a) and the derivative $\partial(T \cdot \chi)/\partial T$ (b) for ZFC case.

Open symbols correspond to ZFC data while closed symbols indicate FC data.

The presence of the second phase can be seen from the variation of the magnetization as a function of the *dc*-applied field, H , in the ZFC condition at different temperatures. The corresponding hysteresis curves are presented by Fig. 5-7.

One can see that the sample S_1 exhibits paramagnetic behavior at 50K (Fig. 5). Shifted hysteresis loops are observed for temperatures below T_c . At 6.6 K the coercive field is about 1600 Oe, much less than that observed value 4600 Oe for the

multidomain single crystal Mn_3O_4 [1]. The saturation magnetization M_s was not reached even at 30 kOe applied magnetic field, but it can be calculated from the $m(1/H)$ plot at $1/H \rightarrow 0$. Thus the saturation magnetization value obtained M_s is about 40 emu/g.

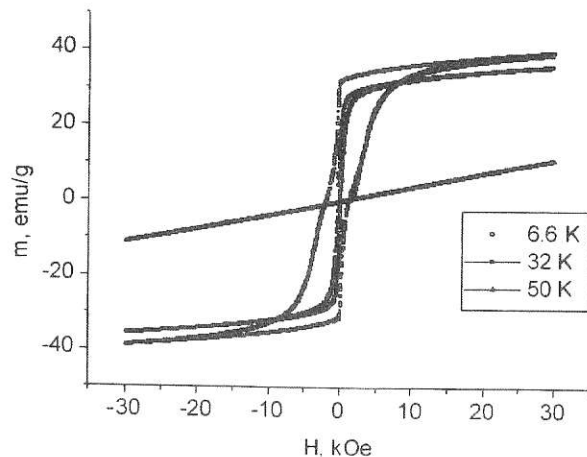


Fig. 5. Hysteresis loops of the sample S_1 at 6.6, 32 and 50 K.

For the sample S_2 a linear (as in paramagnets) dependence of m vs H was observed at 80 K and more high temperatures (Fig. 6). Hysteresis loops at 65 and 50 K represent an example of a mixture of antiferromagnetic and paramagnetic phases. Below 41 K the loops are the result of a mixture of magnetordered phases with different coercivities that produces the so-called "wasp-waisted" hysteresis loops. At 4 K (fig. 7) the coercive field (~400 Oe) is significantly reduced with respect to the corresponding value of the sample S_1 . The difference in the observed coercive field values cannot be attributed to the size effect because for nanoparticles Mn_3O_4 a coercivity increases when the particle size decreases due to an increase in surface anisotropy [5]. Thus the coercivity change must be determined by other consequences of the mechanical activation.

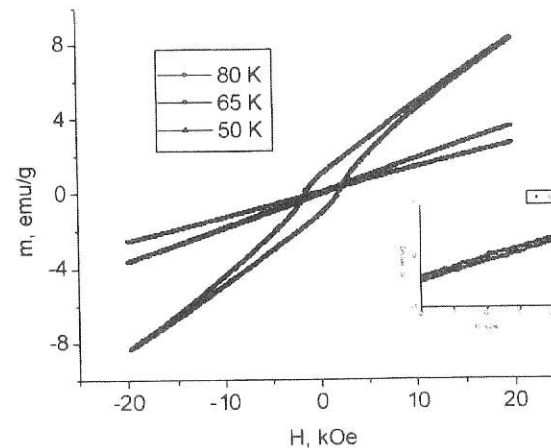


Fig. 6. Hysteresis loops of the sample S_2 at 50, 65 and 80 K. Insert shows the dependence $m(H)$ at 65 K around $H=0$.

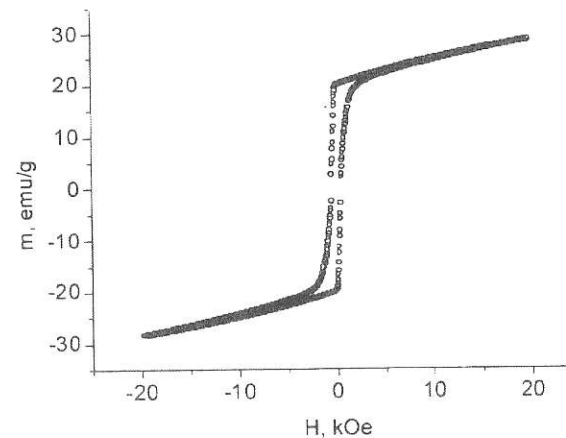


Fig. 7. Hysteresis loop of the sample S_2 at 4 K.

CONCLUSION

We have studied the magnetic properties of the original coarse-grained and mechanically activated Mn_3O_4 powders. It was shown that in both powders the PM-FiM phase transition takes place at $T_c(S_1) = 43\text{ K}$ and $T_c(S_2) = 41\text{ K}$. At that the

mechanical activation of powder is confirmed by the significant decrease in the saturation magnetization value and the coercive field. The magnetic measurements revealed also that in mechanically activated Mn_3O_4 the added phase transition at 80 K is expressed more distinctly. The effect is explained by the presence of second phase in oxide, which was not identified by diffraction method. In compliance with results of [6] one can think that the oxide powders present core/shell structures with Mn_2O_4 core and $\alpha - Mn_2O_3$ shell and the contribution of the shell in magnetic properties is more significant for mechanoactivated sample.

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MODIFYING THE PHYSICO-CHEMICAL PROPERTIES OF $YBa_2Cu_3O_{6+\delta}$ BY "SOFT" HYDRATION

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ABSTRACT

A comprehensive study of $YBa_2Cu_3O_{6+\delta}$ oxide, subjected to a "soft" hydration (exposure at small values of p_{H_2O}) by a special technique has been performed. The material modified in this way acquires a unique property: namely, it intensively absorbs components of the gas atmosphere: O_2 , N_2 , Ar , H_2O и CO_2 . It has been shown that, at least the first four of them enter into the crystal lattice of yttrium-barium cuprate, filling the vacant oxygen positions. Magnetic measurements revealed the coexistence of magnetically ordered and diamagnetic regions in the modified yttrium barium cuprate.

Introduction.

In the work (1) we considered the influence of atmospheric components, embedded into $YBa_2Cu_3O_{6+\delta}$ oxide during storage in air, on its redox properties. It was found, the sample containing water and carbon dioxide in the structure in quantities less than definite level, reveals abnormally high kinetics of oxygen exchange with gas phase at 400°C. Based on these and similar data the technology allowing to obtain material with high diffusion properties was established (2). The hydration of the oxide in the atmosphere with low humidity ("soft" hydration) was the main part of this technology. We supposed, this treatment leads to the transformation of "classical" forms of $YBa_2Cu_3O_{6+\delta}$ into a new, hitherto unknown (below: a modified form of yttrium-barium cuprate, or M-YBC).

The purpose of this work is to find new unique physicochemical properties of the modified $YBa_2Cu_3O_{6+\delta}$ oxide. The main attention of the work is focused on obtaining information about the microstructure and chemical activity of M-YBC using method of proton magnetic resonance and low-temperature magnetic measurements.

Experimental.

The object of study has been modified by technology (2) under the following conditions: $t = 25^\circ C$; $p_{O_2} = 20$ kPa; $p_{H_2O} = 110 \pm 5$ Pa. According to the X-ray diffraction analysis, the modified and the initial phases have the same type of crystal lattice (orthorhombic syngony, space group Pmmm) and negligible differences in unit cell parameters. Investigation of gas absorption kinetics in M-YBC crystal lattice was performed in isothermal conditions at 25°C in air with a constant $p_{CO_2} = 0.03$ kPa and varying the value of the elasticity of water vapor: $p_{H_2O} = 1.0 + 2.3$ kPa. Figure 1 compares the variation of sample mass on the exposure time under fixed external parameters recorded for the modified and the original YBC-oxides.