RADIATION CHANGES OF STRUCTURE AND MAGNETIC PROPERTIES OF BARIUM HEXAFERRITE

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Abstarct. The effect of gamma irradiation and electron irradiation on the crystal structure and magnetic properties of barium hexaferrite $BaFe_{12}O_{19}$ (solid-phase synthesis) was studied. Irradiations caused changes in the ratio of crystalline phases and crystallite sizes, which resulted in changes in the main parameters of the hysteresis loop: coercive force, residual magnetization, saturation magnetization. These changes were non-monotonic depending on the dose, especially immediately after irradiation. In particular, the saturation magnetization measured at 300 K after γ-irradiation of the sample with a dose of $2.1 \cdot 10^7$ P decreased from the initial value of 52.5 to ~ 40.2 emu/g.

Keywords: *barium hexaferrite, gamma irradiation, electron irradiation, crystal structure, magnetic properties*

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INTRODUCTION

For practical purposes, ferrites are one of the most interesting classes of materials in terms of magnetic properties [1]. Depending on the crystal structure, ferrites are divided into 4 main types: spinel ferrites, garnet ferrites, hexaferrites, and orthoferrites [2]. Each of the structure types has its own characteristic advantages. The combination of a number of unique characteristics makes it possible to apply them in a variety of fields. For example, ferrites are widely used in magnetic information recording and magnetic field shielding systems [3]. In our work, we used hexagonal barium ferrites with the structure of magnetoplumbite $BaFe_{(12)}O_{19}$. From the practical point of view, the attractiveness of barium hexaferrite is due to the high values of Curie temperature, saturation magnetization, and magnetic permeability. The large value of electrical resistivity together with excellent corrosion and chemical resistance makes these materials promising for applications in various microwave electronics devices [4]. The technical design of ferrite devices determines the principle of operation, purpose, frequency range and permissible power level, as well as the design and size of elements in microwave devices in the frequency range from 1 to 100 GHz [5, 6].

Studies of barium hexaferrites have also shown their high thermal stability. Due to this property, another potential area of their applications is biomedicine. Prosthetics, magnetic therapy of cancerous tumors, and point drug delivery are among the promising areas for research [7, 8].

New opportunities open up when using ferrites in the development of composite materials of a new class - multiferroics, possessing simultaneously several types of ordered structure, both magnetic and electrical [9, 10].

It is known that the magnetic characteristics of a material are determined at the synthesis stage [11, 12]. Since these or those properties can be, depending on the intended application, both advantages and disadvantages, it is very important to synthesize the magnetic material in the right way. Hexagonal barium ferrites can be obtained by a number of developed methods, among which the most popular are solid-phase synthesis [13], autocombustion [14], mechanical alloying and activation [15], and ceramic method [16]. In the present work, the samples were obtained by solid-phase synthesis.

The demand for barium hexaferrites makes it necessary to study their magnetic properties under various conditions. One of the new directions is the study of changes in magnetic properties of barium hexagonal ferrites as a result of radiation exposure. It is well known that irradiation with electrons, ions, ionizing particles, gamma-quanta can significantly change the structural, mechanical and magnetic properties of the irradiated material. For magnetic materials such studies are few (see [17, 18, 19] and references in these papers), and for ferrites we know only a single attempt of irradiation with neutrons [20] and a study of the absorption capacity of γ-irradiation [21]. The main mechanism of irradiation effect is the appearance of radiation defects, but in addition, heating to high temperatures and, for gamma irradiation, photoeffect and Compton scattering play an important role. Irradiation can initiate the emergence of long-range magnetic order due to the emergence of magnetic moments on defects or broken bonds, the transition from antiferromagnetic to ferrimagnetic state due to discompensation of magnetic moments of sublattices during defect formation [22], or changes in the magnetic properties of ferrites during ionization of iron ions in $Fe^{2+}$and

Fe^{3+}states possessing different magnetic moments, or changes in the magnetic moment of sublattices during chaotization of the distribution of Fe ions. The prospectivity of studies of the effect of different types of radiation exposure on the properties of ferrites is due to the fact that radiation exposure can purposefully change their structural and magnetic properties both during and after fabrication, optimizing them for a specific task.

On the other hand, the importance of this research is determined by the rapid development of the space industry [23, 24]. More and more space vehicles, stations and satellites equipped with complex and sensitive devices are launched into the near-Earth space with elevated radiation levels. Ensuring correct operation of devices under such conditions requires a detailed understanding of the effect of cosmic and solar radiation on the structural and magnetic properties of materials. Since gamma and electron irradiation are dominant in near-Earth orbits and are more accessible for safe experiments with ferrites, the purpose of the present work is to study the effect of these types of irradiation on the crystal structure and magnetic properties of barium-based ferrites with complex hexagonal structure.

SAMPLES AND METHODOLOGY

By the method of solid-phase synthesis 10 samples of the same composition were produced. As initial components for synthesis $BaCO_3$, $Fe_{(2)}\ _{O3}$powders with qualification PMA (pure for analysis) were used. The substances were mixed in stoichiometric ratios and grinded in agate mortar to homogeneous state. After grinding, the mixture was pressed into tablets in a metal mold with a diameter of 20 mm in a

laboratory hydraulic press with a force of 5 t/cm^2. The obtained tablets were placed in a high temperature furnace on a platinum substrate to exclude chemical interaction of the synthesized substances with the elements. Synthesis was carried out at 1350 °C for 5 hours, followed by cooling in the furnace until complete cooling. From the obtained blanks of the same composition 10 plates with close dimensions 10× 5× 2 mm^3, suitable for research, were cut out.

Magnetic properties of the samples were measured immediately after irradiation (after one hour) using a Gaussmeter (Gaussmeter Model GM2). Repeated measurements were performed after 6-month relaxation of the crystal lattice of the samples after the formation of initially unstable defects at room temperature on a LakeShore 7407 series VSM vibrating magnetometer (USA) in fields up to 16 kE. For measurements, a small fragment with dimensions of 1 ×5× 2 mm was separated from each plate[3]. The samples were weighed on electronic scales and attached to the magnetometer holder using Teflon tape.

The structure was examined before and after irradiation using a RigakuUltima IV X-ray diffractometer (Cu Kα, 40 kV, 30 mA; λ = 0.1542 nm) at a recording rate of 2° per minute over an angle range of 2θ= 5-90 degrees.

Samples with an area of 1 cm^{2}were irradiated in air in$\gamma^{\text{-field}}$ $^{(60)}$Co with isotropic 4π -geometry at a dose rate of 84 R/s (0.8· 10^{12}quanta/cm^2) at a temperature of 323 K (Institute of Nuclear Physics, Academy of Sciences of Uzbekistan, INP). Irradiation by gamma quanta with energies of 1.17 and 1.33 MeV is sufficient to initiate secondary ionization and, in addition, to excite vibrations of Ba, Fe, and O nuclei, thereby causing

displacements of atoms from the lattice nodes. Electron irradiation was carried out at a gas pedal at an electron energy of 5 MeV and a beam current density of 1 μA/cm^2.

RESULTS AND DISCUSSION

Structural data

The results of X-ray phase analysis (XRF) under irradiation are presented in Fig. *1a* and *1b*. The initial unirradiated sample (black line) is a single-phase structure corresponding to the control spectrum (a set of vertical lines on the abscissa axis) of barium hexaferrite $BaFe_{(12)}O_{19}$. As a result of irradiation, both by gamma quanta and electrons, the appearance of additional phases is observed; in Fig. 1a*,b* they are marked with asterisks and circles.

At irradiation with a convergent γ-beam on the sample (Fig. *1b*), the highest irradiation density inside the ferrite plates is achieved, as a result, the crystal lattice is damaged and heated, which is sufficient for structural-phase transitions. Analysis of the X-ray spectra of barium hexaferrite shows that γ-irradiation with a dose of $2.1 \cdot 10^7$P caused an increase in the volume of the main structural phase $BaFe_{(12)}O_{(19)}$ at the expense of a decrease in the phase $Ba_{(2)}Fe_{(30)}O_{46}$. At the same time, the volume content of the phases $Fe_{(2)}O_3$ and $Fe_{(2.957)}O_4$ remained practically unchanged.

Magnetic properties

Figures 2-4 show the main magnetic characteristics of barium hexaferrite $BaFe_{(12)}O_{19}$ before and after irradiation. For all samples after irradiation, hysteresis loops were measured at room temperature in fields up to 16 kE, from which the main magnetic parameters were determined - saturation magnetization (M_s) , for which we

conditionally take the magnetization in the field of 16 kE, since full saturation in this field is not achieved, residual magnetization (M_r) and coercivity ($H_{c)}$, presented in Table 1. In the calculation, the influence of demagnetizing factor N, taken, based on the parameters of the samples, equal to 0.255, was taken into account. The first row in the table corresponds to the properties of unirradiated samples, while the information for irradiated samples is presented below. Depending on the irradiation dose, significant changes in the main magnetic parameters can be observed.

At low doses of electron irradiation, an insignificant (up to 3%) increase in saturation magnetization is observed (Table 1), and at high doses - a noticeable decrease, up to 10%. At the same time, the coercive force monotonically decreases (Table 1). Apparently, at the initial stage, when the heating of samples is insignificant, the formation of defects leads to the appearance of additional magnetic moments on the broken bonds, but, as one would expect, this effect is insignificant and is at the level of the experimental error. A strong decrease in magnetization under prolonged irradiation is associated with an increase in the concentration of radiation defects. In magnetically hard ferromagnetics, the coercive force is largely determined by the magnitude of the magnetic anisrotropy constant. The slightest displacements of magnetic ions from equilibrium positions or changes in their environment due to defect formation reduce the magnetic anisotropy and, consequently, the coercivity. The non-monotonicity (decrease and increase) of the dose dependence of the coercive force may be related to the competition between magnetically hard and magnetically soft phases in the studied ferrites samples, which continues in the relaxation process after

irradiation. The mechanism of this anomaly requires further investigation by compacting experimental points on the dose and relaxation dependences.

Before gamma-ray irradiation, the magnetization of barium hexaferrite $BaFe_{(12)}O_{19}$was 52.5 eme/g, and after γ-irradiation of the sample with a dose of $2.1\cdot 10^7$P (or irradiation time of 2.7 h), the magnetization decreased to~ 40.2 eme/g (Fig. 3).

What is the reason for the magnetization reduction at low dose of γ-irradiation? We assume the following scenario. At a low dose of γ-irradiation, electron-hole pairs are generated. The momentum imparted to the ions causes them to be displaced from their equilibrium positions, and the temperature of the samples increases only slightly. The first process cannot be responsible for the change in magnetization, since the measurements were made after a long relaxation time, and recombination processes are fast. In turn, ion displacements in the absence of heating can exist for quite a long time, which is confirmed by the data of X-ray diffraction analysis. They can lead to a decrease in the exchange interaction between iron ions and, as a consequence, to a decrease in magnetization. With increasing irradiation dose, this mechanism is leveled off due to both strong heating and significant defect formation. The value of the coercive force during gamma-quantum irradiation (Fig. 4) has a non-monotonic dependence. At a low dose of irradiation (up to 7 h), a sharp decline of the coercivity is observed, then in the future we will investigate it in more detail.

CONCLUSION

Gamma-quantum and electron irradiation have significant and different effects on the structural and magnetic properties of $BaFe_{(12)}O_{19}$ferrites. At irradiation with a

convergent γ-beam on the sample the highest density of γ-irradiation is reached, as a result the crystal lattice is damaged and heated, which is sufficient for structural-phase transitions. Analysis of X-ray structural changes of barium hexaferrite shows that γ-irradiation with a dose of $2.1\cdot 10^7$P caused an increase in the main structural phase $BaFe_{(12)\ O(19)}$at the expense of a decrease in the amount of $Ba_{(2)}Fe_{(30)\ O46}$phase . At the same time, the volume content of $Fe_{(2)\ O3}$and $Fe_{(2.957)\ O4}$phases remained practically unchanged. Studies of the magnetic properties of Wa-hexaferrite at 300 K showed that before irradiation their magnetization was 52.5 eme/g, and after γ-irradiation of the sample with a dose of $2.1\cdot 10^7$P the saturation magnetization decreased to~ 40.2 eme/g. With further increase in dose, the magnetization magnetization increases monotonically but does not reach its initial value. At low doses of electron irradiation, the saturation magnetization increases and decreases to 47.3 eme/g with further increase of irradiation dose.

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FIGURE CAPTIONS

Fig. 1. XRF analysis results for electron-irradiated samples at electron energy of 5 MeV and beam current density of 1 μA/cm$^{(2)\,(a)}$; for gamma-irradiated samples at dose rate of 84 R/s and T=323 K (b).

Fig. 2. Magnetic hysteresis loops of the original unirradiated sample (Wa), gamma-irradiated (55 h) and electron-irradiated (800 s) samples of hexaferrite $BaFe_{(12)}O_{19}$.

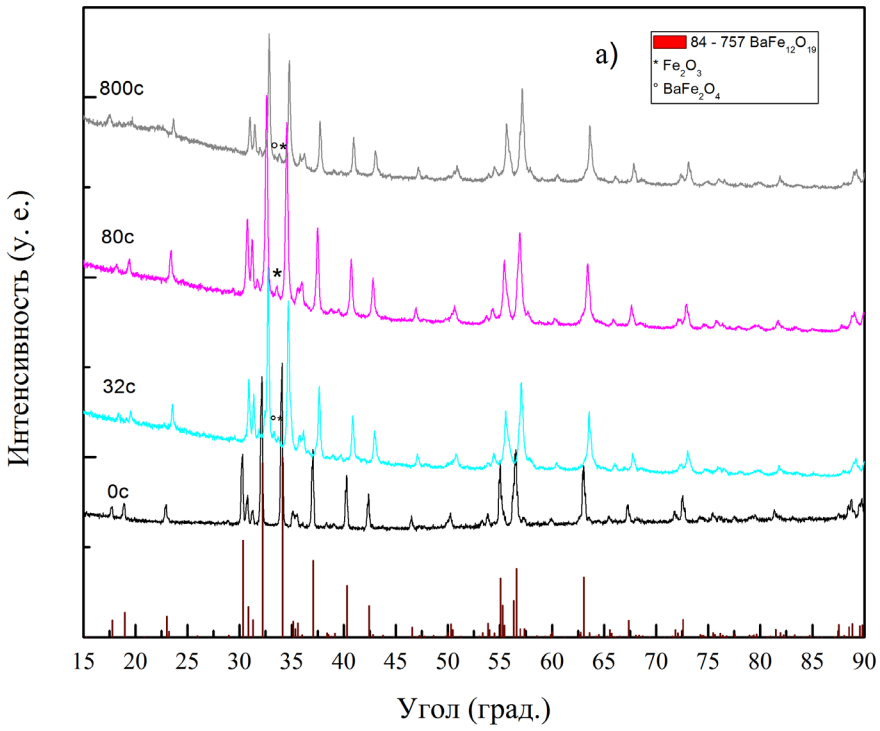
Fig. 3. Variation of magnetization of $BaFe_{(12)}O_{19}$hexaferrite as a function of irradiation time for gamma-irradiated samples.

Fig. 4. Variation of the coercivity of $BaFe_{(12)}O_{19}$hexaferrite as a function of irradiation time for gamma-irradiated samples.

Table 1: Main magnetic parameters of $BaFe_{(12)}O_{19}$hexaferrite samples irradiated with electrons and gamma quanta.

Dose	time	*m*, mg	Gauss measurement immediately after irradiation $H \parallel H_{Earth}$, Hs Gs/g, ($\times 10^{-4}$)	*H* = 12 kE, *H* = 16 kE 6 months after irradiation		
				M_s, eme/g	M_r, eme/g	H_c, E
0	-	70.65	2.6	52.5	23.8	1060
Electron dose irradiation ($\times 10^{14}$, cm^{-2})						
2.0	32 c	138.9	1.2 8.6	53.9	25.7	1008
5.0	80 c	68.7	2.9 42	50.3	28.1	958
50	800 c	115	1.3 11	47.3	22.2	699
Gamma irradiation dose ($\times 10^6$, P)						
0.8	2.7 ч	62.2	2.6 42	40.2	24.5	794

2.1	7 ч	71.2	1.7 24	44.5	19	420
5.0	17 ч	79	2.7 34	47.4	23.4	663
10	33 ч	104.7	55 525	49.6	18.8	451
17	55 ч	74.7	2.2 29	48.9	19.8	523



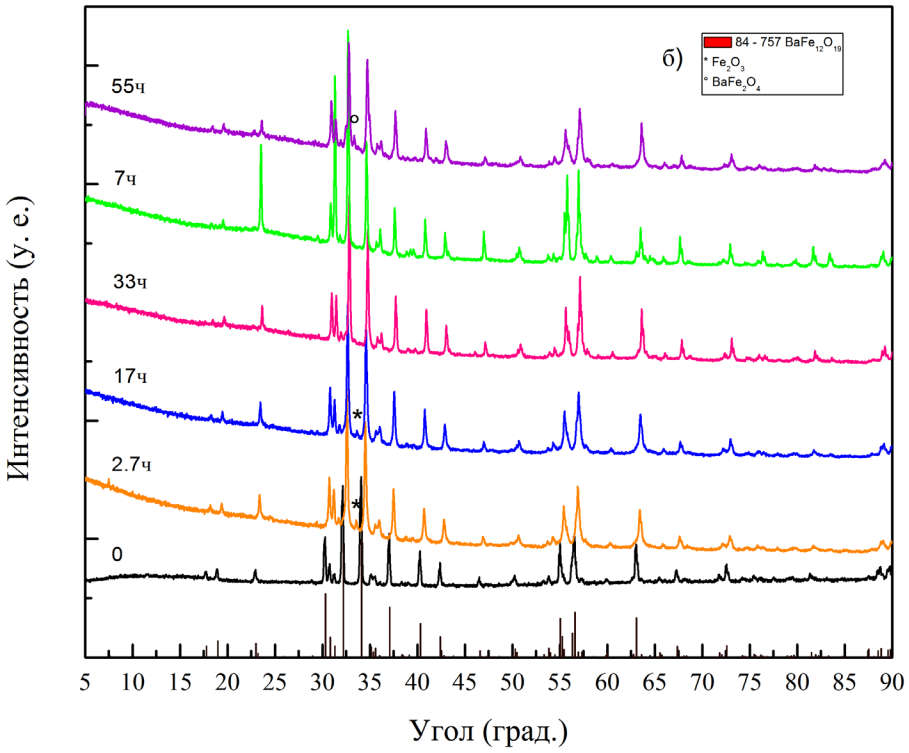

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Fig. 1.

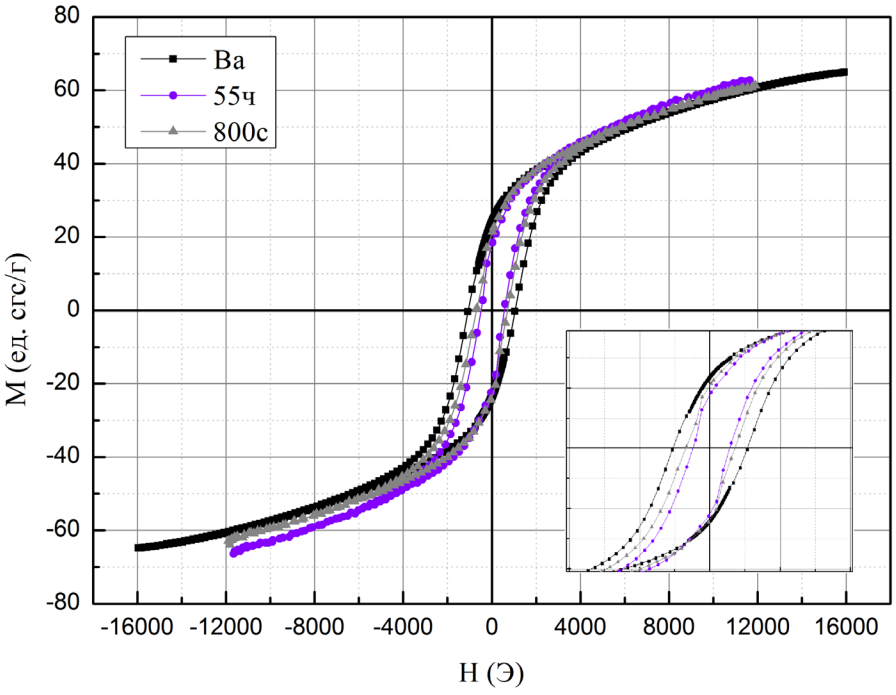
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Fig. 2.

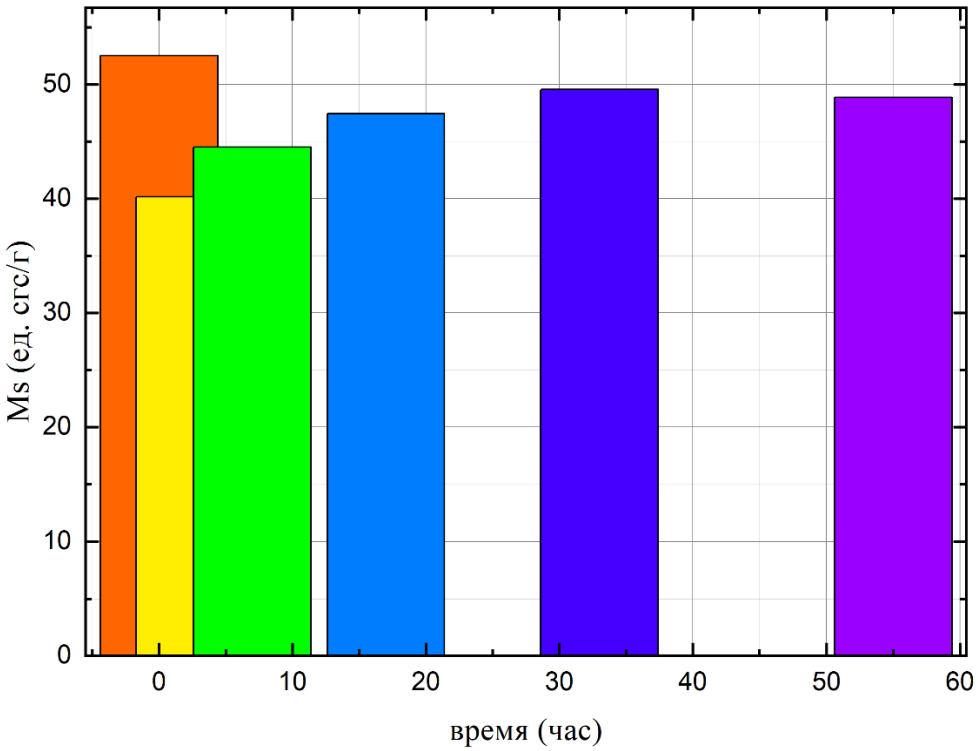
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Fig. 3.

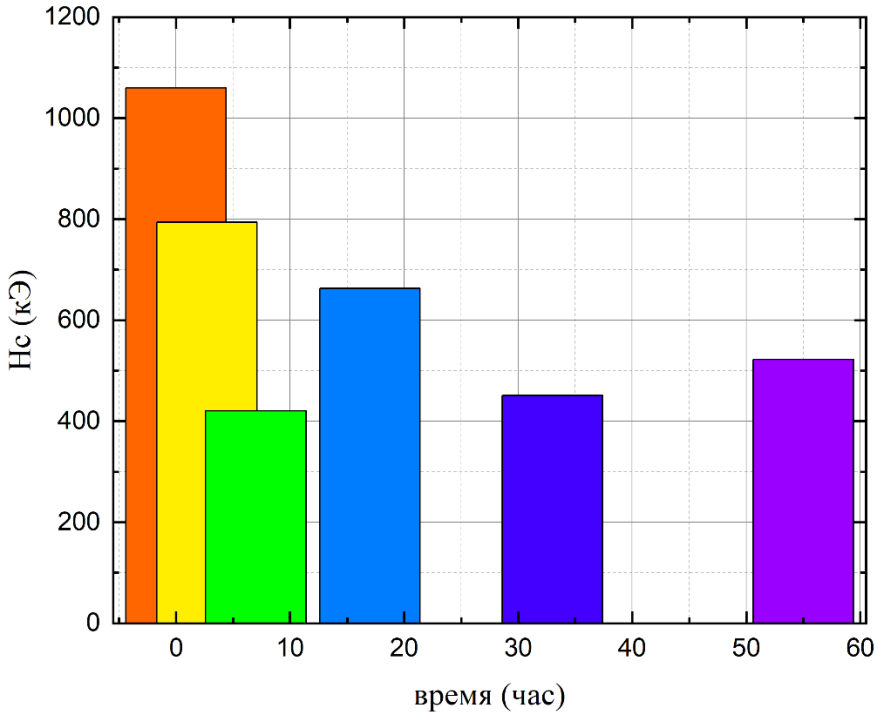
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Fig. 4.