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МАГНИТОТЕПЛОВЫЕ СВОЙСТВА ФЕРРИТА МЕДИ

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В данной работе проведен направленный синтез феррита меди ($CuFe_2O_4$) методом соосаждения из растворов избытком щелочи при температуре 373 К. Методами сканирующей электронной микроскопии и рентгенофазового анализа исследована кристаллическая структура и морфология поверхности феррита меди. Проведено отнесение характеристических пиков дифрактограмм в соответствии с базой данных JCPDS. Показано, что феррит меди (II) кристаллизуется в структуре кубической шпинели. Приведены микрофотографии синтезированных образцов данного феррита при разном увеличении. Установлено, что частицы феррита меди (II) состоят из конгломератов кристаллов с различным размером отдельных зерен. На приведенных микрофотографиях видно, что наблюдается небольшой разброс по размерам. Средний размер частиц находится в диапазоне 100-200 нм. С помощью дифференциального сканирующего калориметра динамического теплового потока получена температурная зависимость удельной теплоемкости образцов феррита меди в диапазоне температур 273 - 373 К. С использованием оригинальной микрокалориметрической установки в интервале температур 288 – 346 К и при изменении индукции магнитного поля от 0 до 1,0 Тл получены термодинамические характеристики - магнитокалорический эффект (МКЭ) и изменение энтропии (ΔS) в процессе намагничивания феррита меди (II). Было установлено, что величина МКЭ растет с увеличением индукции магнитного поля и уменьшается с ростом температуры. Было обнаружено, что температурные зависимости магнитокалорического эффекта и удельной теплоемкости имеют экстремальный характер. В области комнатных температур (308-315 К) наблюдается максимум магнитокалорического эффекта и минимум удельной теплоемкости. Подобное, ранее не известное, аномальное поведение магнитотепловых свойств феррита меди II обнаружено впервые.

Ключевые слова: феррит меди, рентгенофазовый анализ, электронная микроскопия, магнетокалорический эффект, удельная теплоемкость, магнитное поле

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MAGNETOTHERMAL PROPERTIES OF COPPER FERRITE

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In this work, we carried out the directed synthesis of copper ferrite ($CuFe_2O_4$) by co-precipitation from solutions with an excess of alkali at a temperature of 373 К. The methods of scanning electron microscopy and X-ray phase analysis were used to study the crystal structure and surface morphology of copper ferrite. The ratio of the characteristic peaks of the diffractogram was carried out in accordance with the JCPDS database. It is shown that copper (II) ferrite crystallizes in the structure of the cubic spinel. Microphotographs of the synthesized copper ferrite samples at different magnifications are given. It is established that ferrite particles consist of conglomerates of crystals with different sizes of individual grains. Their small scatter in size is observed. The average particle size is in the range of 100-200 nm. Using a dynamic heat flux differential scanning calorimeter, the temperature dependence of the heat capacity of copper ferrite samples was obtained in the temperature range of 273–373 K. Using an original microcalorimetric setup in the temperature range of 288–346 K and with a change in the magnetic field induction from 0 to 1.0 T, thermodynamic characteristics were obtained - the magnetocaloric effect (MCE) and the change in entropy (ΔS) during the magnetization of copper (II) ferrite. It was found that with an increase in the magnitude of the magnetic field, the magnitude of the MCE increases and decreases with increasing temperature. It was found that the temperature dependences of the magnetocaloric effect and specific heat have an extreme character. In the region of room temperatures (308–315 K), a maximum of the magnetocaloric effect and a minimum of the specific heat are observed. This previously unknown anomalous behavior of the magneto-thermal properties of copper II ferrite was discovered for the first time.

Key words: copper ferrite, X-ray phase analysis, electron microscopy, magnetocaloric effect, specific heat capacity, magnetic field

Ferrites are a combination of iron oxides Fe_2O_3 with oxides of other transition metals, including copper, zinc, cobalt, nickel, manganese, magnesium. They constitute a special group of magnetically ordered materials in which there are crystallographically and magnetically nonequivalent sublattices, the presence of which determines the magnetic properties of ferrimagnets, which differ from the properties of ferro- and antiferromagnets.

Compounds of oxides of transition elements have high chemical resistance and relatively low cost. This leads to their widespread use as magnetic materials in electronics, radio engineering and computer technology, since they combine high magnetic susceptibility with semiconductor or dielectric properties. Spinels based on copper (II) ferrite are magnetic materials [1, 2] they are used as catalysts, electrodes, gas sensitive sensors [3, 4].

Currently, active studies of the magnetocaloric effect (MCE) on various magnetically ordered substances are underway [5-7]. The essence of this phenomenon lies in the adiabatic temperature change in the sample when the external magnetic field changes as a result of the redistribution of internal energy between the system of magnetic atoms and the crystal lattice.

The study of the magnetocaloric properties of magnets is very important for solving the fundamental problems of magnetism, which are associated with the possibility of obtaining information about magnetic transitions in magnetic materials and about the magnetic state of matter. The MCE is accompanied by a change in such quantities as entropy, heat capacity and thermal conductivity [8].

From the point of view of the study and application of magnetothermal properties, magnets with magnetic phase transitions in the region of room temperatures are promising. Magnetic transitions are accompanied by a magnetocaloric effect and heat capacity anomalies. These substances include various compounds of ferrites [9-11].

Previously, we conducted a study of the adsorption capacity, elemental composition of copper ferrite, carried out its dispersion analysis, and determined the specific surface of this ferrite [12, 13]. In this work, we continue studying the properties of CuF_2O_4 by magnetocaloric methods.

EXPERIMENTAL PART

The synthesis of highly dispersed copper ferrite was carried out by chemical condensation in a thermostated vessel for an hour at a temperature of 370 K. A dark brown CuF_2O_4 precipitate was obtained by coprecipitation from aqueous solutions of (Cu^{2+}) and (Fe^{3+}) ions with an excess of KOH solution. The precipitate was decanted into a magnetic field and dried under vacuum for five hours. Dry powder particles reacted to the action of a magnetic field [14].

The phase composition of obtained structures was analyzed by X-ray diffraction (X-ray diffractometer D2 Advance, Brucker, CuK_α source).

Morphological studies of the nanostructured sample were carried out using a Quattro S scanning electron microscope (Thermo Fisher Scientific, Czech Republic).

The heat capacity of the samples was measured on a dynamic heat flux differential scanning calorimeter DSC 204 F1 Phoenix (Netzsch, Germany). The heat capacity measurement error was 1.5%. The temperature range of scanning in accordance with microcalorimetric studies was chosen from 273 to 373 K.

The microcalorimetric method was used to study the MCE of copper ferrite using an original microcalorimeter [15, 16]. A sample of copper ferrite in the form of an aqueous suspension was placed in a microcalorimetric cell with an isothermal shell. The cell was located between the poles of an electromagnet. The magnetic field induction in the gap varied from 0 to 1 T. The sensitivity of the setup was 2.10-5 K. The error in measuring the MCE did not exceed 2%. To check the reliability of the calorimeter, calibration was carried out using metallic gadolinium (98% chemical purity).

The magnetocaloric effect ΔT_{MCE} was determined from the heat balance equation (1):

$$Q_{MCE} = m_{(M)}C_{P(M)}\,\Delta T_{MCE}, \qquad (1)$$

where Q_{MCE} is the amount of heat released when a magnetic field is applied to a magnet under isothermal conditions; $m_{(M)}$, $C_{p(M)}$ – mass, specific heat capacity of copper ferrite.

The amount of heat Q_{MCE}, which is released as a result of the magnetocaloric effect, was determined calorimetrically according to equation (2), comparing Q_{MCE} with the Joule heat (QJ) introduced into the calorimeter as a result of calibration by electric current:

$$Q_{MCE} = Q_J\,(\Delta T/\Delta T_J), \qquad (2)$$

where Q_J is the amount of Joule heat introduced into the calorimeter during calibration by electric current, ΔT_J is the change in temperature of the calorimetric system as a result of the injected Joule heat, ΔT is the change in temperature of the calorimeter system as a result of the MCE.

The entropy change ΔS under the action of a magnetic field on a magnetic sample was calculated using the equation (3):

$$\Delta S = -\,C_{p(M)}\,\Delta T_{MCE}/T, \qquad (3)$$

where T is the absolute temperature, $C_{p(M)}$ is the specific heat capacity of copper ferrite.

RESULTS AND DISCUSSION

Fig. 1 show micrographs of the synthesized copper ferrite samples at different magnifications. It can be seen from the photographs that the nanoparticles consist of conglomerates of crystals with different sizes of individual grains; there is a small scatter in size. The dried powder consists of aggregated quasi-spherical particles with a rough surface. Comparative morphological analysis of particle projections on all obtained micrographs showed that the average particle fine size is in the range of 100-200 nm.

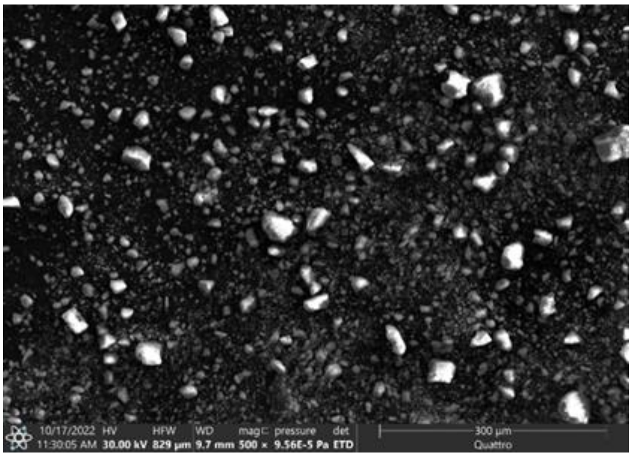
When analyzing the diffraction patterns, it was found that the peaks 2θ = 18.5, 35.6, 38.8, 43.0, 62.2 (Fig. 2), in accordance with the JCPDS database (77-0010), refer to single-phase crystalline copper ferrite and confirms the presence of reflections of the cubic spinel. The data obtained in our work correspond to the data for CuF_2O_4 [17].

Among the ferrites of transition metals, $CuFe_2O_4$ is the only one that is ferromagnetic of room temperature [17, 18].

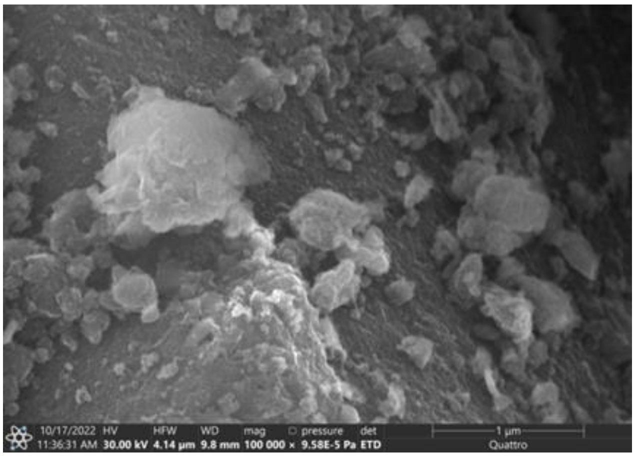
It was previously established that the presence of a λ-point at 663 K corresponds to the transition from cubic to tetragonal. The peak at about 743 K is that associated with the magnetic transition of this material [19, 20].

When analyzing experimental data, the temperature dependence of the specific heat capacity (Fig. 3) has a continuous character. The dependence is a monotonically increasing function of temperature with increasing slope, which is typical for this kind of spinels. In the temperature range from 283 to 373 K, the specific heat capacity varies from 0.665 to 0.762 J/g·K. Attention is drawn to a small minimum in the region of 313 K. These changes in the heat capacity are reflected in the temperature dependence of the MCE.

When studying the temperature dependences of polycrystalline copper ferrite for all thermodynamic characteristics ΔT_{MCE} and ΔS_M (Fig.4, 5), there is a decrease in thermodynamic values with increasing temperature. However, in the region of 313 K, a sharp maximum was found on all temperature dependences of the thermodynamic quantities. With an increase in the magnetic field induction (B) from 0 to 1.0 T, the maximum value of ΔT_{MCE} increases and reaches a value of 0.035K.



a



b

Fig. 1. Micrographs of the synthesized copper ferrite sample at various magnifications. Scale: a -X300; б-X1

Рис. 1. Микрофотографии синтезированного образца феррита меди при различном увеличении. Масштаб: а – X300; б – X1

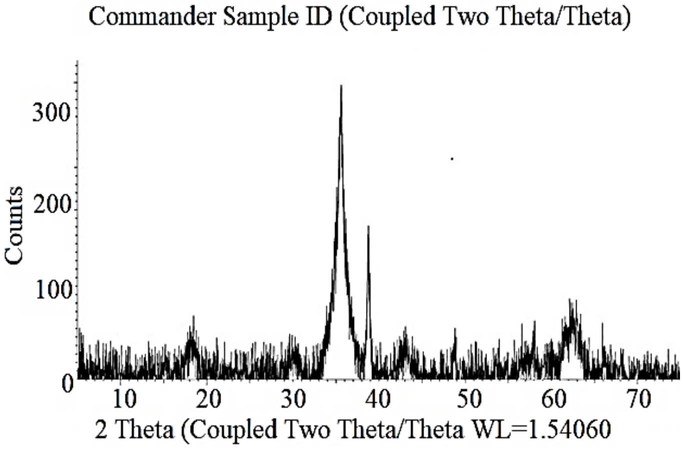


Fig. 2. X-ray pattern of copper ferrite

Рис. 2. Рентгенограмма феррита меди

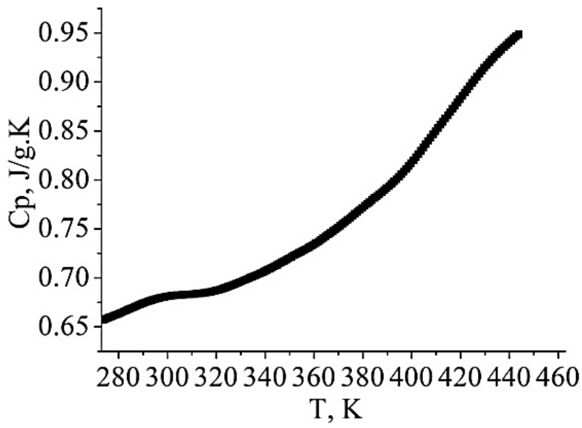


Fig. 3. Temperature dependence of the specific heat capacity of copper ferrite

Рис. 3. Температурная зависимость удельной теплоемкости феррита меди

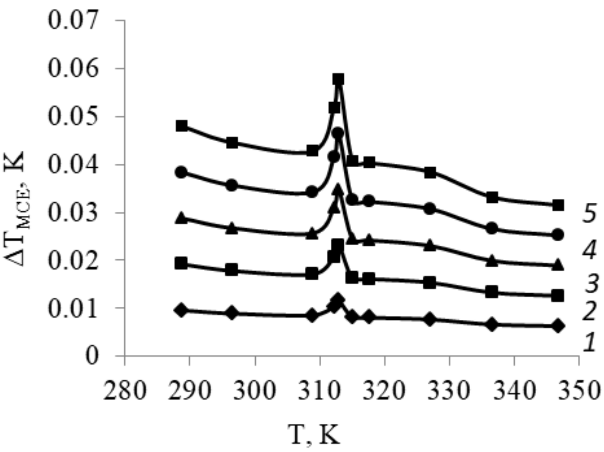


Fig. 4. Temperature dependence of the magnetocaloric effect (ΔT_{MCE}) in magnetic fields with induction (B): 1- 0.2; 2- 0.4; 3- 0.6; 4- 0.8; 5- 1.0 T

Рис. 4. Температурная зависимость магнитокалорического эффекта ($\Delta T_{МСЭ}$) в магнитных полях с индукцией (В): 1- 0,2; 2- 0,4; 3- 0,6; 4- 0,8; 5- 1,0 Т

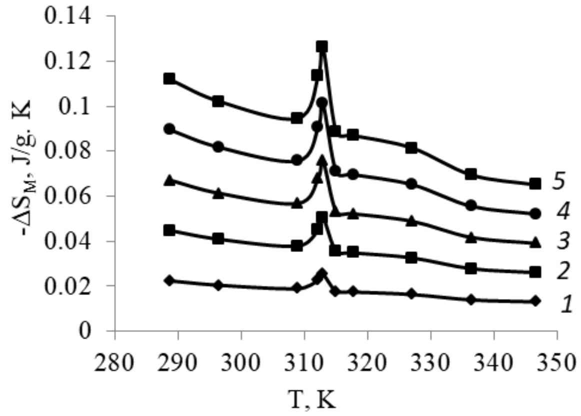


Fig. 5. Temperature dependence of entropy change (ΔS_M) in various magnetic fields with induction (B): 1- 0.2; 2- 0.4; 3- 0.6; 4- 0.8; 5- 1.0 T

Рис. 5. Температурная зависимость изменения энтропии (ΔS_M) в различных магнитных полях с индукцией (B): 1- 0,2; 2- 0,4; 3- 0,6; 4- 0,8; 5- 1,0 T

A similar anomalous behavior in the region of 313 K is also observed in the temperature dependence of the heat capacity. Apparently, the detected anomaly of thermodynamic characteristics is associated with changes occurring in the crystal lattice of copper ferrite and requires additional studies.

CONCLUSION

In this work, copper ferrite was synthesized by co-precipitation from aqueous solutions of Cu^{2+} and Fe^{3+} ions with an excess of KOH. The crystal structure was studied by X-ray phase analysis and the chemical composition of copper ferrite samples was established. Using scanning electron spectroscopy, the surface morphology of $CuFe_2O_4$ crystallites was studied. The particle size is in the range of 100-200 nm. The heat capacity of copper ferrite samples was determined by differential scanning calorimetry. In the temperature range from 283 to 373 K, the specific heat capacity varies from 0.665 to 0.762 J/g·K. The magnetocaloric effect and the change in the entropy of the samples were determined by the microcalorimetric method on the original installation in the temperature range of 288-346 K and in a magnetic field of 0-1.0 T. Based on the temperature dependences of the MCE, changes in entropy and heat capacity, an anomalous behavior of copper ferrite in the region of 313 K was found. On the temperature dependences of the MCE and ΔS at 313 K, maxima are observed, and on the temperature dependence of the specific heat, a minimum of values. With an increase in the magnetic field induction, the maxima increase. The detected anomaly of thermodynamic characteristics is associated with changes occurring in the crystal lattice of copper ferrite and requires additional studies.

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The authors declare the absence a conflict of interest warranting disclosure in this article.

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ЛИТЕРАТУРА

1. **Karimipourfard D., Eslamloueyan R., Mehranbod N.** Novel heterogeneous degradation of mature landfill leachate using persulfate and magnetic $CuFe_2O_4$/RGO nanocatalyst. *Proc. Safety Environ. Protect.* 2019. V. 131. P. 212-222. DOI: 10.1016/j.psep.2019.09.009.
2. **Narang S.B., Pubby K.** Nickel Spinel Ferrites: A Review. *J. Magn. Magn. Mater.* 2021. V. 2(1). P. 167163. DOI: 10.1016/j.jmmm.2020.167163.
3. **Шабельская Н.П., Егорова М.А., Арзуманов А.В.** Получение композиционных материалов на основе феррита кобальта (II) для очистки водных растворов. *Изв. вузов. Химия и хим. технология.* 2021. Т. 64. Вып. 2. С. 95-102. DOI: 10.6060/ivkkt.20216402.6215.
4. **Saravanakumar B., Ramachandran S.P., Ravi G., Ganesh V., Ramesh K. Guduru, Yuvakkumar R.** Electrochemical performances of monodispersed spherical $CuFe_2O_4$ nanoparticles for pseudocapacitive applications. *Vacuum.* 2019. V. 168. P. 108798. DOI: 10.1016/j.vacuum.2019.108798.
5. **Шабельская Н.П., Кухарева В.П., Михайличенко С.Н., Шилкина Л.А., Таланов М.В., Ульянов А.К.** Особенности синтеза и фазообразование в системе NiO-FeO-Fe_2O_3-

REFERENCES

1. **Karimipourfard D., Eslamloueyan R., Mehranbod N.** Novel heterogeneous degradation of mature landfill leachate using persulfate and magnetic $CuFe_2O_4$/RGO nanocatalyst. *Proc. Safety Environ. Protect.* 2019. V. 131. P. 212-222. DOI: 10.1016/j.psep.2019.09.009.
2. **Narang S.B., Pubby K.** Nickel Spinel Ferrites: A Review. *J. Magn. Magn. Mater.* 2021. V. 2(1). P. 167163. DOI: 10.1016/ j.jmmm.2020.167163.
3. **Shabelskaya N.P., Egorova M.A., Arzumanova A.V., Yakovenko E.A., Zababurin V.M., Vyaltsev A.V.** Preparation of composite materials based on cobalt (II) ferrite for purification of aqueous solutions. *ChemChemTech [Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.].* 2021. V. 64. N 2. P. 95-102. DOI: 10.6060/ivkkt.20216402.6215.
4. **Saravanakumar B., Ramachandran S.P., Ravi G., Ganesh V., Ramesh K. Guduru, Yuvakkumar R.** Electrochemical performances of monodispersed spherical $CuFe_2O_4$ nanoparticles for pseudocapacitive applications. *Vacuum.* 2019. V. 168. P. 108798. DOI: 10.1016/j.vacuum.2019.108798.
5. **Shabel'skaya N.P., Kukhareva V.P., Mikhailichenko S.N., Shilkina L.A., Talanov M.V., Ulyanov A.K.** Features

Cr_2O_3. *Изв. вузов. Сев.-Кавк. регион. Техн. науки.* 2015. № 2. С. 91 – 95. DOI: 10.17213/0321-2653-2015-2-91-95.

6. **Bohra M., Sahoo S.C.** Large magnetocaloric effect at Verwey point in nanocrystalline Fe_3O_4 thin films. *J. Alloys Compd.* 2017. V. 699. P. 1118-1121. DOI: 10.1016/j.jallcom.2017.01.013.
7. **Zhong J., Liu W., Jiang L., Yang M., Morais P.C.** Real-time magnetic nanothermometry: The use of magnetization of magnetic nanoparticles assessed under low frequency triangle-wave magnetic fields. *Rev. Sci. Instrum.* 2014. V. 85. P. 094905. DOI: 10.1063/1.4896121.
8. **McMichael R.D., Shull R.D., Swartzendruber L.J., Bennett L.H., Watson R.E.** Magnetocaloric effect in superparamagnets. *J. Magn. Magn. Mater.* 1992. V. 111. P. 29-33. DOI: 10.1016/0304-8853(92)91049-Y.
9. **Shabel'skaya N.P.** Synthesis and properties of binary spinels in a NiO–CuO–Fe_2O_3–Cr_2O_3 system. *Glass Phys. Chem.* 2017. V. 43. N 3. P. 240-245. DOI: 10.1134/S1087659617030129.
10. **Балагуров А.М., Бобриков И.А., Мащенко М.С., Сангаа Д., Симкин В.Г.** Структурный фазовый переход в $CuFe_2O_4$. *Кристаллография*. 2013. Т. 58. № 5. С. 696-703. DOI: 10.7868/S0023476113040048.
11. **Иванова Н.М., Соболева Е.А., Висурханова Я.А., Мулдахметов З.** Электрохимическое получение Fe–Cu-композитов на основе феррита меди (II) и их электрокаталитические свойства. *Электрохимия*. 2020. Т. 56. № 7. С. 579-590. DOI: 10.31857/s0424857020070038.
12. **Балмасова О.В., Королев В.В.** Адсорбция жирных кислот из растворов органических растворителей на поверхности высокодисперсных ферримагнетиков. *Изв. вузов. Химия и хим. технология.* 2009. Т. 52. Вып. 7. С. 52-56.
13. **Балмасова О.В., Королев В.В., Яшкова В.И.** Изотермы адсорбции-десорбции олеиновой кислоты из раствора четыреххлористого углерода на поверхности высокодисперсных ферритов. *Журн. физ. химии.* 2010. Т. 84. № 1. С. 82-86. DOI: 10.1134/S0036024410010152.
14. **Завадский А.Е. Железнов К.Н., Рамазанова А.Г., Балмасова О.В., Королев В.В., Яшкова В.И.** Влияние магнитного поля и температуры на процесс кристаллизации ультрамикроскопических частиц магнетита. *Докл. АН.* 1998. Т. 361. № 3. С. 362-365.
15. **Korolev V.V., Korolev D.V., Ramazanova A.G.** The calorimetric method of evaluating the performance of magnetocaloric materials. *J. Therm. Anal. Calorim.* 2019. V. 136. P. 937-941. DOI: 10.1007/s10973-018-7704-y.
16. **Korolev V.V., Romanov A.S., Aref'ev I.M.** Magnetocaloric Effect and Heat Capacity of Ferrimagnetic Nanosystems: Magnetite-Based Magnetic Liquids and Suspensions. *J. Phys. Chem.* 2006. V. 80. P. 464-466. DOI: 10.1134/S0036024406030277.
17. **Егорова М.А., Шабельская Н.П., Раджабов А.М., Чернышева Г.М., Таранушич В.А., Забабурин В.М., Вяльцев А.В., Ульянова В.А.** Получение и свойства ферррита и хромита меди (Ⅱ). *Изв. вузов. СКР. Техн. науки.* 2021. № 2. С. 69-74. DOI: 10.17213/1560-3644-2021-2-69-74.
18. **Andreenko A.S., Belov K.P., Nikitin S.A.** Magnetocaloric effects in rare land magnets. *Usp. Phys. Nauk.* 1989. N 158. P. 553-579. DOI: 10.3367/UFNr.0158.198908a.0553.
19. **Кузнецов М.В., Морозов Ю.Г., Белоусова О.В.** Синтез наночастиц феррита меди. *Неорг. Матер.* 2013. Т. 49. № 6. С. 606-615. DOI: 10.7868/S0002337X13050060.
20. **Inoue T., Iida S.** Specific Heats of Copper Ferrite. *J. Phys. Soc. Jpn.* 1958. N 13. P. 656. DOI: 10.1143/JPSJ.13.656A.

of synthesis and phase formation in the NiO-FeO-Fe_2O_3-Cr_2O_3 system. *Izv. Vuzov. Sev.Kavk. Region. Tekhn. Nauki*. 2015. N 2. P. 91 – 95 (in Russian). DOI: 10.17213/0321-2653-2015-2-91-95.

6. **Bohra M., Sahoo S.C.** Large magnetocaloric effect at Verwey point in nanocrystalline Fe_3O_4 thin films. *J. Alloys Compd.* 2017. V. 699. P. 1118-1121. DOI: 10.1016/j.jallcom.2017.01.013.
7. **Zhong J., Liu W., Jiang L., Yang M., Morais P.C.** Real-time magnetic nanothermometry: The use of magnetization of magnetic nanoparticles assessed under low frequency triangle-wave magnetic fields. *Rev. Sci. Instrum.* 2014. V. 85. P. 094905. DOI: 10.1063/1.4896121.
8. **McMichael R.D., Shull R.D., Swartzendruber L.J., Bennett L.H., Watson R.E.** Magnetocaloric effect in superparamagnets. *J. Magn. Magn. Mater.* 1992. V. 111. P. 29-33. DOI: 10.1016/0304-8853(92)91049-Y.
9. **Shabel'skaya N.P.** Synthesis and properties of binary spinels in a NiO–CuO–Fe_2O_3–Cr_2O_3 system. *Glass Phys. Chem.* 2017. V. 43. N 3. P. 240-245. DOI: 10.1134/S1087659617030129.

10. **Balagurov A.M., Bobricov I.A., Maschenko M.S., Sangaa D., Simkin V.G.** Structural phase transition in spinel $CuFe_2O_4$. *Crystallography*. 2013. V. 58. N 5. P. 696-703. DOI: 10.7868/S0023476113040048.
11. **Ivanova N.M., Soboleva E.A., Visurkhanova Ya.A., Muldakhmetov Z.** Electrochemical preparation of Fe–Cu composites based on copper (II) ferrite and their electrocatalytic properties. *Electrochemistry*. 2020. V. 56. N 7. P. 579-590. DOI: 10.31857/s0424857020070038.
12. **Balmasova O.V., Korolev V.V.** Adsorption of fatty acids from organic solvents solutions on surface of superfine ferromagnetics. *ChemChemTech [Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.]*. 2009. V. 52. N 7. P. 52-56 (in Russian).
13. **Balmasova O.V., Korolev V.V., Yashkova V.I.** Oleic acid adsorption–desorption isotherms on the surface of high–dispersity ferrites from a solutions in carbon tetrachloride. *Russ. J. Phys. Chem. A.* 2010. V. 84. N 1. P. 76-80. DOI: 10.1134/S0036024410010152.
14. **Zavadsky A.E. Zheleznov K.N., Ramazanova A.G., Balmasova O.V., Korolev V.V., Yashkova V.I.** The influence of magnetic field and temperature on the crystallization process of ultramicroscopic magnetite particles. *Dokl. AN.* 1998. V. 361. N 3. P. 362-365 (in Russian).

15. **Korolev V.V., Korolev D.V., Ramazanova A.G.** The calorimetric method of evaluating the performance of magnetocaloric materials. *J. Therm. Anal. Calorim.* 2019. V. 136. P. 937-941. DOI: 10.1007/s10973-018-7704-y.
16. **Korolev V.V., Romanov A.S., Aref'ev I.M.** Magnetocaloric Effect and Heat Capacity of Ferrimagnetic Nanosystems: Magnetite-Based Magnetic Liquids and Suspensions. *J. Phys. Chem.* 2006. V. 80. P. 464-466. DOI: 10.1134/S0036024406030277.

17. **Egorova M.A., Shabelskaya N.P., Radzhabov A.N., Chernysheva G.M., Taranushich V. A., Zababurin V.M., Vyaltsev A.V., Ulyanova V.A.** Preparation and properties of ferrite and chromite of copper (Ⅱ). *Izv. Vuzov Sev. Kavk. Region. Tekhn. Nauki.* 2021. N 2. P. 69-74. DOI: 10.17213/1560-3644-2021-2-69-74.

18. **Andreenko A.S., Belov K.P., Nikitin S.A.** Magnetocaloric effects in rare land magnets. *Usp. Phys. Nauk.* 1989. N 158. P. 553-579. DOI: 10.3367/UFNr.0158.198908a.0553.

19. **Kuznetsov M.V., Morozov Yu.G., Belousova O.V.** Synthesis of copper ferrite nanoparticles. *Neorg. Mater.* 2013. V. 49. N 6. C. 606-615 (in Russian). DOI: 10.7868/S0002337X13050060.

20. **Inoue T., Iida S.** Specific Heats of Copper Ferrite. *J. Phys. Soc. Jpn.* 1958. N 13. P. 656. DOI: 10.1143/JPSJ.13.656A.

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