



Original Research Paper

Thermally induced changes in the magnetic properties of iron oxide nanoparticles under reducing and oxidizing conditions

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ABSTRACT

Application of iron oxide nanoparticles in the fields of water purification, biomedicine or chemistry often requires controlled magnetic properties that can be modified by changing temperature and redox conditions. Therefore, this work investigates the changes in the magnetic properties of iron oxide nanoparticles in the FeOOH – Fe₂O₃ – Fe₃O₄ system (i.e. hematite, goethite, lepidocrocite, maghemite and magnetite) at heating under reducing and oxidizing conditions. The results show that heat treatment of hematite and goethite in the presence of a reducing agent (5% starch) leads to their conversion into high magnetic magnetite. The starting temperature of transformation is approximately 350 °C for both samples. The magnetization increases to 86 Am²/kg for hematite reduced at 700 °C and to 88 Am²/kg for goethite reduced at 900 °C. An intense reaction occurs within the first 10 min and then the conversion process decelerates. Thermal treatment of lepidocrocite under both oxidizing and reducing conditions leads to an increase in magnetization due to the formation of maghemite and magnetite, respectively. Regardless of the redox conditions, the formation of magnetic phase begins at a temperature of 250 °C and is associated with the formation of maghemite from lepidocrocite. Under oxidizing conditions, the magnetization begins to decrease at 350 °C, which is associated with the conversion of maghemite to hematite. On the contrary, under reducing conditions, the magnetization of lepidocrocite increases up to 900 °C, which is associated with the formation of magnetite. Maximum values of magnetization are 36 Am²/kg for maghemite obtained at 350 °C, and 88 Am²/kg for magnetite obtained at 900 °C from lepidocrocite. With the help of conventional heating, the magnetic properties of IONs can be altered by phase transformations in the FeOOH – Fe₂O₃ – Fe₃O₄ system. Temperature and redox conditions are the two most important factors controlling the transformation pathways and the magnetic properties of the resulting IONs.

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1. Introduction

In recent decades, numerous researchers have paid attention to the study of iron oxide nanoparticles (IONs). Magnetic IONs can be used in the fields of water purification, biomedicine, optoelectronics, and chemistry [1–6]. Such nanoparticles with a large surface area and unique magnetic properties are a potential adsorbent for the removal of hazardous substances from water such as nitrates [7], strontium [5], dyes [8], heavy metals [9]. Magnetic adsorbents can be easily removed from water by using a magnetic field gradient [10]. Magnetic nanoparticles with coated surface are promising materials that can be used for biomedical applications, including targeted drug delivery, magnetic resonance imaging

(MRI) enhancement, magnetic hyperthermia and thermoablation, bioseparation and biosensing [11–13].

The practical application of iron oxide nanoparticles is often determined by their magnetic properties. A characteristic feature of most iron minerals is the diversity of their phase transitions and transformations, which results in corresponding changes in magnetic properties (e.g., magnetic susceptibility or Curie temperature).

It is well known that hematite (α -Fe₂O₃) is resistant to high temperatures under oxidizing conditions, whereas under reducing conditions it can be converted to magnetite (Fe₃O₄) or maghemite (γ -Fe₂O₃). However, the conditions of this transformation and the magnetic properties of the obtained sample are poorly defined. Hanesch et al. [14] used thermomagnetic analysis to show that the presence of organic matter leads to the formation of maghemite or magnetite from hematite above 450 °C. Ellid et al. [15] found that chemical reduction of hematite with starch for 2 h at

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300 °C leads to the formation of magnetite and a small fraction of hematite. In our previous work [16], we have shown that the reduction of synthetic and natural hematite begins at about a temperature of 350 °C. The obtained magnetic samples revealed a similar Curie temperature but very different mass magnetization, which suggests a higher conversion fraction for the synthetic mineral due to the larger surface area.

When heated under oxidizing conditions, goethite (α -FeOOH) is converted to hematite. Because both minerals are antiferromagnetic, the magnetic susceptibility changes slightly. In contrast, under reducing conditions, goethite is converted to magnetite with a possible intermediate hematite formation. Experiments with the reduction of goethite are mainly devoted to natural coarse particles of goethite iron ores [17–19]. The reduction of nanoscale goethite has been studied in several papers. For example, Hanesch et al. [14] found that in the presence of glucose, goethite begins to turn into a high-magnetic mineral at 420 °C. We also compared the reduction of natural and synthetic goethites in [20] using thermomagnetic analysis. The reduction with starch results in the formation of magnetite at 270 °C from synthetic goethite and at 500 °C from brown goethite ore. An increase in the saturation magnetization was observed from $< 1 \text{ Am}^2/\text{kg}$ to $70 \text{ Am}^2/\text{kg}$ for synthetic goethite and to $25 \text{ Am}^2/\text{kg}$ for natural goethite.

Thermal decomposition of lepidocrocite (γ -FeOOH) under oxidizing conditions has been well studied due to the formation of highly magnetic maghemite. Generally, lepidocrocite begins to transform to maghemite at 200 °C [21,22]. Gehring and Hofmeister [21] found that the structural conversion of lepidocrocite to maghemite starts at about 200 °C and is completed around 300 °C. At higher temperatures, maghemite is converted into hematite. The effect of reducing agents on the transformation of lepidocrocite has not been sufficiently studied. Hanesch et al. [14] have suggested that in the presence of organic carbon, the reaction of lepidocrocite starts at slightly lower temperatures and is somewhat stronger, but the end product is the same.

Since the available data on the control of the magnetic properties of iron oxide nanoparticles under the influence of oxidizing and reducing conditions are inconsistent and incomplete, additional systematic studies can greatly assist the synthesis of nanoparticles with predetermined magnetic characteristics, as well as the selection of precursors and operating conditions, which can be significant in laboratory and industrial settings.

Therefore, the goal of this work is to study the changes in the magnetic properties of iron oxide nanoparticles (i.e. hematite, goethite, lepidocrocite) when heated under both reducing and oxidizing conditions. The structure and magnetic properties of the obtained samples are investigated by thermomagnetic analysis, scanning electron microscopy, X-Ray diffraction and magnetometry measurements.

2. Materials and methods

2.1. Synthesis of initial IONs

All reagents used in the synthesis were commercial products. Synthesis of lepidocrocite included dissolving 16.68 g of ferrous sulfate in 300 ml of distilled water with a magnetic stirrer. The pH of the solution varied in the range of 6.7–6.9. During the synthesis, 1 M sodium hydroxide was gradually added in order to maintain the pH at the required level. The solution was incubated at a room temperature accompanying with air blowing through the solution. The obtained precipitate was washed three times with distilled water using centrifuge and dried in the thermostat to constant mass. The duration of the experiment was 4 h and terminated when the color of the solution became yellow.

A sample of synthetic goethite was synthesized using a solution of 0.48 M sodium hydrogen carbonate (50 ml) that was slowly poured under intensive stirring into the solution of 0.4 M iron (III) nitrate (50 ml), and then the resulting suspension was heated up to boiling and then cooled down. Afterwards, the solution of 5 M sodium hydroxide in 100 ml of distilled water was added into the suspension. The formed precipitate was stored in a thermostat for 24 h at a temperature of 90 °C. During this time, the precipitate was completely turned into crystalline light-yellow goethite.

Hematite sample was synthesized through the thermal decomposition of synthetic goethite at 400 °C during 30 min in a quartz reactor isolated from atmospheric oxygen.

2.2. IONs thermal treatment

The initial samples weighing up to 0.3 g were heated in a furnace at temperatures from 100 to 900 °C and for a time interval of 10–60 min. These conditions were chosen because most redox reactions of iron minerals occur within this temperature range, and 10–60 min is usually sufficient to evaluate the effect of time at the laboratory level.

Hematite and goethite were heated under reducing conditions, whereas lepidocrocite was treated under both reducing and oxidizing conditions. The 5% of starch was mixed with the samples to simulate reducing conditions. The reducing conditions were used as an additional controller of the magnetic properties of iron oxide nanoparticles due to the reaction Fe^{2+} to Fe^{3+} and vice versa. Previous experience in addition to theoretical calculations indicates that 5% of starch is more than sufficient to completely convert iron oxides and hydroxides into magnetite.

The heat treatment was carried out in a quartz reactor with a diameter of 1 cm. After each phase transformation, the saturation magnetization was measured with an estimated error of $1.5 \text{ Am}^2/\text{kg}$.

2.3. Methods of characterization

The crystal structure and magnetic properties of initial and resulting samples have been described using X-Ray diffraction, scanning electron microscopy, thermomagnetic analysis and magnetometer measurements.

X-ray diffraction analysis was carried out using diffractometer DRON-3 M in filtered emission $\text{CuK}\alpha$ ($\lambda = 0.154184 \text{ nm}$) with recording geometry by Bregg-Brentano. The diffraction data cards were used for XRD phase diagnostics by d-spacing detecting.

Magnetization measurements as a function of an applied field was performed by magnetometer with the Hall sensors. The analysis of the samples was carried out at a room temperature. An external magnetic field of magnetometer varied in the range of $0 \pm 0.45 \text{ T}$.

Thermomagnetic curves were obtained with a custom-built facility consisting of a digital balance with a built-in permanent magnet. An applied permanent magnetic field of 300 mT was used. The samples were heated and cooled in a quartz reactor isolated from atmospheric oxygen. The rate of heating and cooling of the samples was $65 \text{ }^\circ\text{C}/\text{min}$. Thermomagnetic data include derivative thermomagnetic curves (DTMC) and integral thermomagnetic curves (TMC).

A field emission scanning electron microscope JSM-6700F (“JEOL”) was used to determine the morphology and size of iron oxide nanoparticles. Before imaging, the samples were coated with a platinum film of 30 Å in thickness using sputtering method. Operating conditions of imaging were as follows: SE mode, 10 kV accelerating voltage and 0.65 nA beam current.

3. Results and discussion

3.1. Characterization of initial IONs

The initial synthetic minerals were characterized using scanning electron microscopy, X-ray diffraction, magnetometry and thermomagnetic measurements. X-Ray diffraction analysis showed that goethite and hematite were pure substance, while lepidocrocite contained traces of goethite (Fig. 1). XRD-patterns of synthetic goethite and lepidocrocite revealed broadening of diffraction peaks corresponding to small crystallite sizes. Hematite had narrower diffraction peaks than iron hydroxides.

Scanning electron microscopy showed that synthetic goethite was represented by aggregates consisting of needle-like particles having a length of 300–500 nm and a width of about 100 nm (Fig. 1a). Morphological observations of synthetic hematite also

revealed unusual acicular particles, which are typical of goethite, not hematite (Fig. 1b). This is in agreement with Cornell and Schwertmann's [23] assertion that hematite obtained at low temperatures retains the acicular morphology of crystals of the goethite precursor, but at $>600\text{ }^{\circ}\text{C}$ the sintering process results in irregular hematite particles. Fig. 1c also shows that lepidocrocite reveals the common morphology of flattened scales of several hundred nanometers in length and up to 100 nm in width.

The magnetic properties of all original samples were typical for these minerals. Goethite, lepidocrocite and hematite had low magnetization due to antiferromagnetic coupling. The hematite had a slightly higher magnetic moment ($0.34\text{ Am}^2/\text{kg}$) and a Neel temperature of $\sim 680\text{ }^{\circ}\text{C}$, indicating a weak ferromagnetic moment [24].

Therefore, relatively pure minerals with crystalline structures and nanometer sizes with common morphology and magnetic properties represent all of the starting IONs.

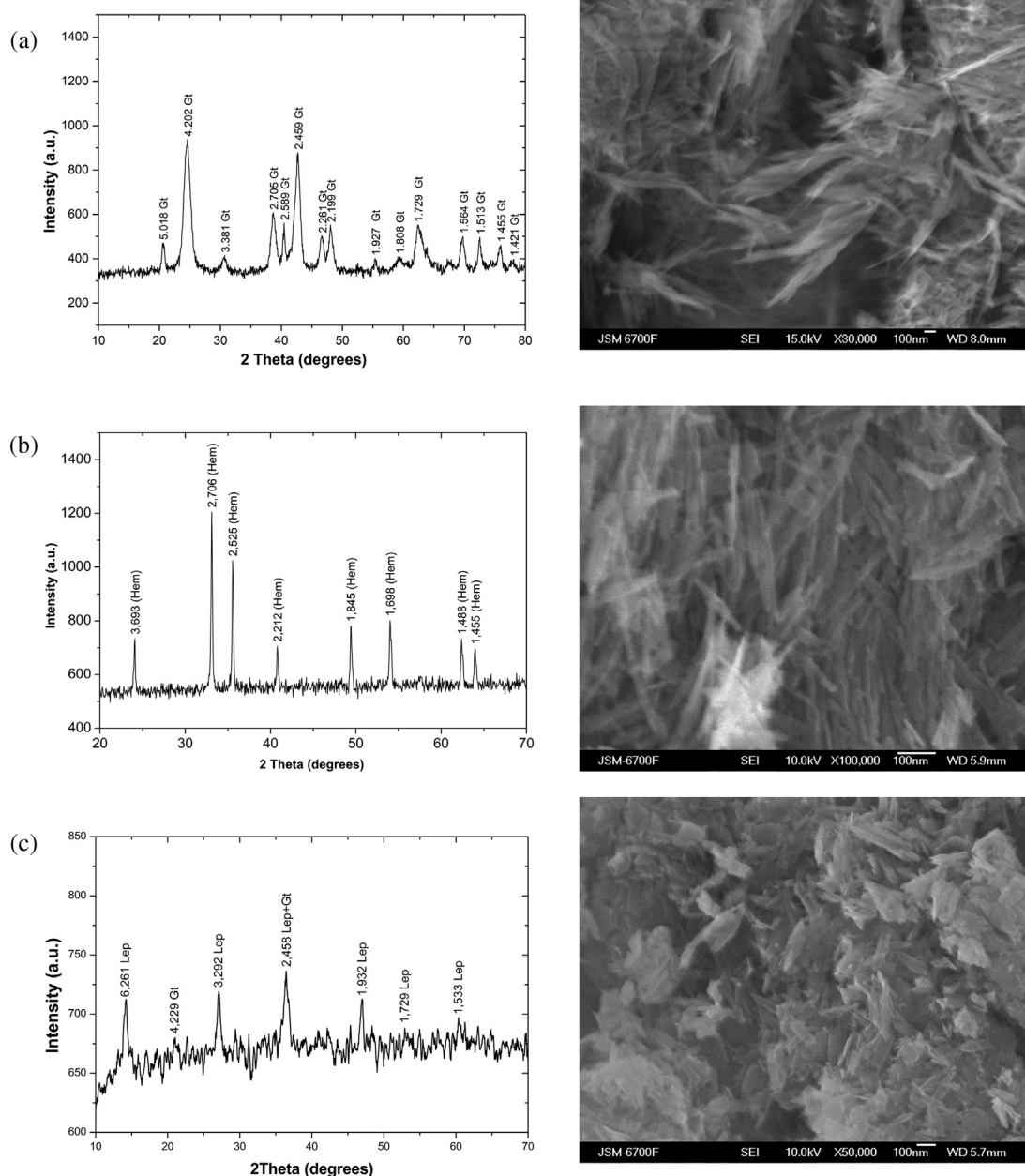
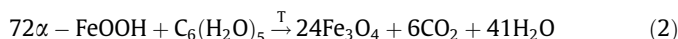
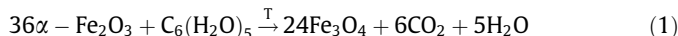


Fig. 1. XRD-patterns and SEM-images of initial IONs: (a) goethite, (b) hematite, (c) lepidocrocite.

3.2. Temperature dependence of magnetization

The initial iron oxide nanoparticles were treated at temperatures 100–900 °C and for a time of 10 min. Hematite and goethite were heated under reducing conditions, which were provided by mixing with 5% of starch. After treatment, magnetization of the samples was measured in a field of 450 mT. The dependence of magnetization on annealing temperature for hematite and goethite heated under reducing conditions for 10 min is shown in Fig. 2.

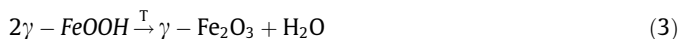
Thermal treatment of both hematite and goethite led to an increase in magnetization (Fig. 2). This increase in magnetization was caused by the partial reduction of Fe^{3+} to Fe^{2+} with carbon and the subsequent formation of magnetite (Eqs. (1) and (2)).



The starting temperature of the reduction of goethite and hematite was about 350 °C, and a further increase in temperature was accompanied by a further rapid increase in magnetization. However, the reaction rate decelerated at approximately 500 °C for both minerals. The magnetization increased to 86 Am^2/kg for hematite reduced at 700 °C and to 88 Am^2/kg for goethite reduced at 900 °C.

For hematite reduction, there was a slight decrease in magnetization at temperatures above 700 °C. This can be interpreted as a partial oxidation of the newly formed magnetite due to the change of reducing to oxidizing conditions. The oxidizing conditions were triggered by more active consumption of starch when reacting with hematite than with goethite.

The magnetization of synthetic lepidocrocite started to increase at a temperature of 250 °C under both reducing and oxidizing conditions (Fig. 3). Under oxidizing conditions, the increase in magnetization is explained by the formation of highly magnetic maghemite (Eq. (3)).



The saturation magnetization reached its maximum value of 36 Am^2/kg after heating lepidocrocite at 350 °C under oxidizing conditions. At higher temperatures, the magnetization started to decrease due to the conversion of maghemite into hematite. The magnetization dropped almost completely at 500 °C.

Under reducing conditions, the magnetization of lepidocrocite started to increase at the same temperature as under oxidizing

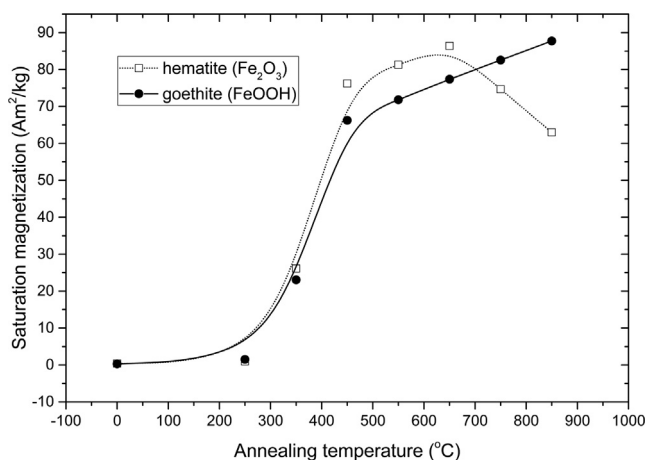


Fig. 2. The dependence of magnetization on annealing temperature for hematite and goethite heated under reducing conditions for 10 min.

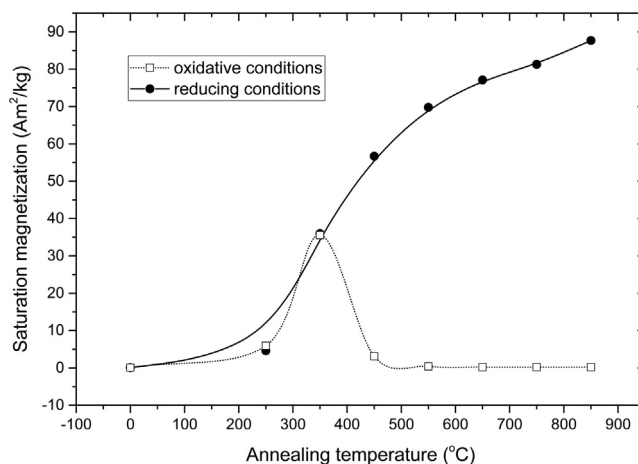
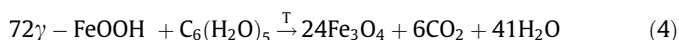


Fig. 3. The dependence of magnetization on annealing temperature for lepidocrocite heated under reducing and oxidizing conditions for 10 min.

conditions. Since the values of magnetization are very close under both reducing and oxidizing conditions up to 300 °C, it can be assumed that the increase in magnetization was also caused by the formation of maghemite. Above 300 °C, the effect of the reducing conditions became apparent as the magnetization continued to increase up to 900 °C (Fig. 3).

The reducing conditions led to the formation of magnetite (Eq. (4)) by means of the reduction of hematite, which was formed during the conversion of maghemite. Therefore, we assume the formation of magnetite from lepidocrocite through the intermediate formation of maghemite and hematite. Consequently, the conversion of lepidocrocite to magnetite can be described by the following generalized equation:



The magnetization of the reduced lepidocrocite increased to 85 Am^2/kg , and the dependence of magnetization at high temperatures was similar to that observed for goethite in Fig. 2.

3.3. Time dependence of magnetization

Fig. 4 shows the dependence of magnetization on annealing time for the reduction of hematite and goethite at 500 °C. A sharp increase in magnetization occurred during the first 10 min of the reaction for both samples. Further increase in annealing time imposed a small effect on magnetization. However, a slight decrease in magnetization was observed for the sample of hematite. This can be explained by a partial oxidation of magnetite due to more active combustion of the reducing agent in the presence of hematite. The saturation magnetization of magnetite, obtained by goethite reduction, remained stable throughout the interval of 10–60 min.

Fig. 5 displays the temperature dependence of magnetization of lepidocrocite heated under reducing conditions at 500 °C and under oxidizing conditions at 350 °C. In both experiments, the magnetization usually increased during the first 10 min of the reactions, followed by a slowdown for both reactions. Although for the conversion of lepidocrocite to maghemite, there is still a gradual increase in magnetization during annealing time of 10–60 min.

Consequently, the reduction of hematite, goethite, and lepidocrocite with starch is significantly more dependent on temperature than on annealing time, since the reaction decelerates after approximately 10 min of heating.

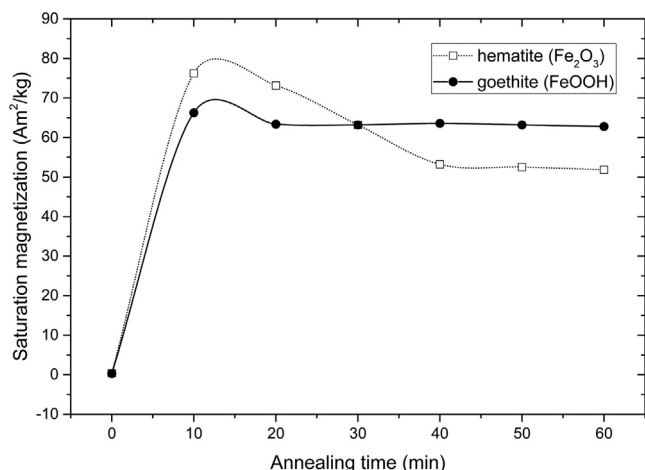


Fig. 4. The dependence of magnetization on annealing time for hematite and goethite heated under reducing conditions at 500 °C.

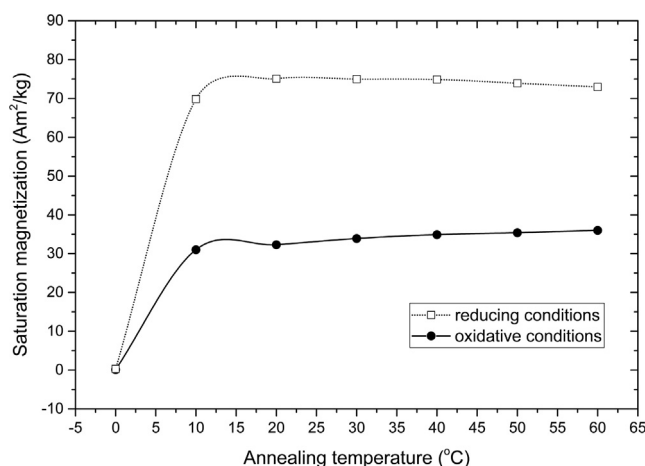


Fig. 5. The dependence of magnetization on annealing time for lepidocrocite heated under reducing conditions at 500 °C and oxidizing conditions at 350 °C.

3.4. Characterization of transformed nanoparticles

The obtained samples were analyzed using X-Ray diffraction, thermomagnetic analysis, scanning-electron microscopy and magnetometry.

3.4.1. X-ray diffraction and scanning electron microscopy

XRD-pattern of hematite reduced at 900 °C for 10 min indicates the presence of diffraction peaks of magnetite (Fig. 6a). Scanning electron microscopy showed that the morphology of the particles changed from articular to spherical, with different sphere sizes ranging from tens to hundreds of nanometers.

Heat treatment of goethite in the presence of a reducing agent at 900 °C for 10 min also led to its complete conversion into magnetite (Fig. 6b). Electron microscopic imaging showed that needle-like goethite evolved into isometric homogeneous particles of magnetite with an average diameter of 100 nm.

XRD-pattern of the specimen obtained by thermal decomposition of lepidocrocite at 350 °C for 10 min showed that the diffraction peaks of lepidocrocite disappeared and the peaks of the spinel structure attributed to maghemite developed (Fig. 6c). The peaks are characterized by broadening and low intensity, indicating a small crystallite size. Acicular and scaly particles of lepidocrocite retain their morphology when converted into maghemite.

The reduction of lepidocrocite at 900 °C for 10 min led to the appearance of diffraction peaks of magnetite (Fig. 6d). The morphology of the scale lepidocrocite changed to spherical magnetite, locally baked in the form of dumbbells, with an average diameter of 100 nm.

Note that the diffraction pattern of magnetite is close to a pattern of some other minerals with a spinel structure, including maghemite. Hence, it is not always possible to distinguish magnetite from maghemite by X-Ray diffraction. Although the parameters of magnetite and maghemite lattices are almost identical, the thermal stability and Curie temperature of these iron oxides are distinctly different. Therefore, it is possible to clearly differentiate magnetite from maghemite by thermomagnetic analysis.

3.4.2. Thermomagnetic analysis

Thermomagnetic curves of the samples obtained by the reduction of hematite and goethite at 900 °C for 10 min (Fig. 7) are similar to those of pure magnetite. There is a decrease in magnetization as a function of temperature, which is characteristic of all magnetic substances, since the exchange energy associated with the coupling of spin moments decreases. The Curie temperature of the obtained sample was 570 °C for reduced goethite and 565 °C for reduced hematite, approaching the Curie temperature of pure stoichiometric magnetite (580 °C).

Small fluctuations in the magnetization at 200–300 °C may be related to the thermal redistribution of iron ions in the particles. Since the reduction occurs from the surface to the center of particles, this can lead to excess of Fe²⁺ ions on the particle surface and Fe³⁺ in the inner part of magnetite particles.

Fig. 8 shows the thermomagnetic curves of the samples obtained by oxidation and reduction of lepidocrocite at 350 and 900 °C, respectively. For the sample obtained by reduction of lepidocrocite, the Curie temperature is approximately 580 °C, which is in good agreement with a value for pure magnetite. When heated to 650 °C and cooled to ambient temperature, the magnetic moment of the sample remained stable, which also distinguishes magnetite from unstable maghemite.

On the contrary, the magnetization of maghemite obtained from lepidocrocite dropped sharply at 450 °C, which means the conversion of maghemite into hematite. Since the maghemite is unstable when heated, it is not possible to measure the Curie temperature of the sample. On cooling, there is no increase in magnetization, which means a complete conversion of maghemite to hematite.

3.4.3. Magnetometry

The dependence of magnetization on an applied magnetic field for magnetite obtained by the reduction of hematite and goethite is shown in Fig. 9a. The remanence and coercivity are low, implying a soft magnetic behavior. The field in which the saturation was reached was approximately 100 mT, with a slightly higher value for magnetite obtained from hematite than from goethite.

For the samples of maghemite and magnetite obtained from lepidocrocite, hysteresis loops with soft magnetic behavior were detected (Fig. 9b). However, the saturation magnetization as well as the coercivity and remanence are higher for magnetite than for maghemite. Typically, maghemite particles showed lower coercivity than the corresponding magnetite according to its lower anisotropy [25].

4. Discussion

The starting temperatures of transformation, the influence of time and temperature on the conversion kinetics, and the values of mass magnetization of the samples obtained are discussed.

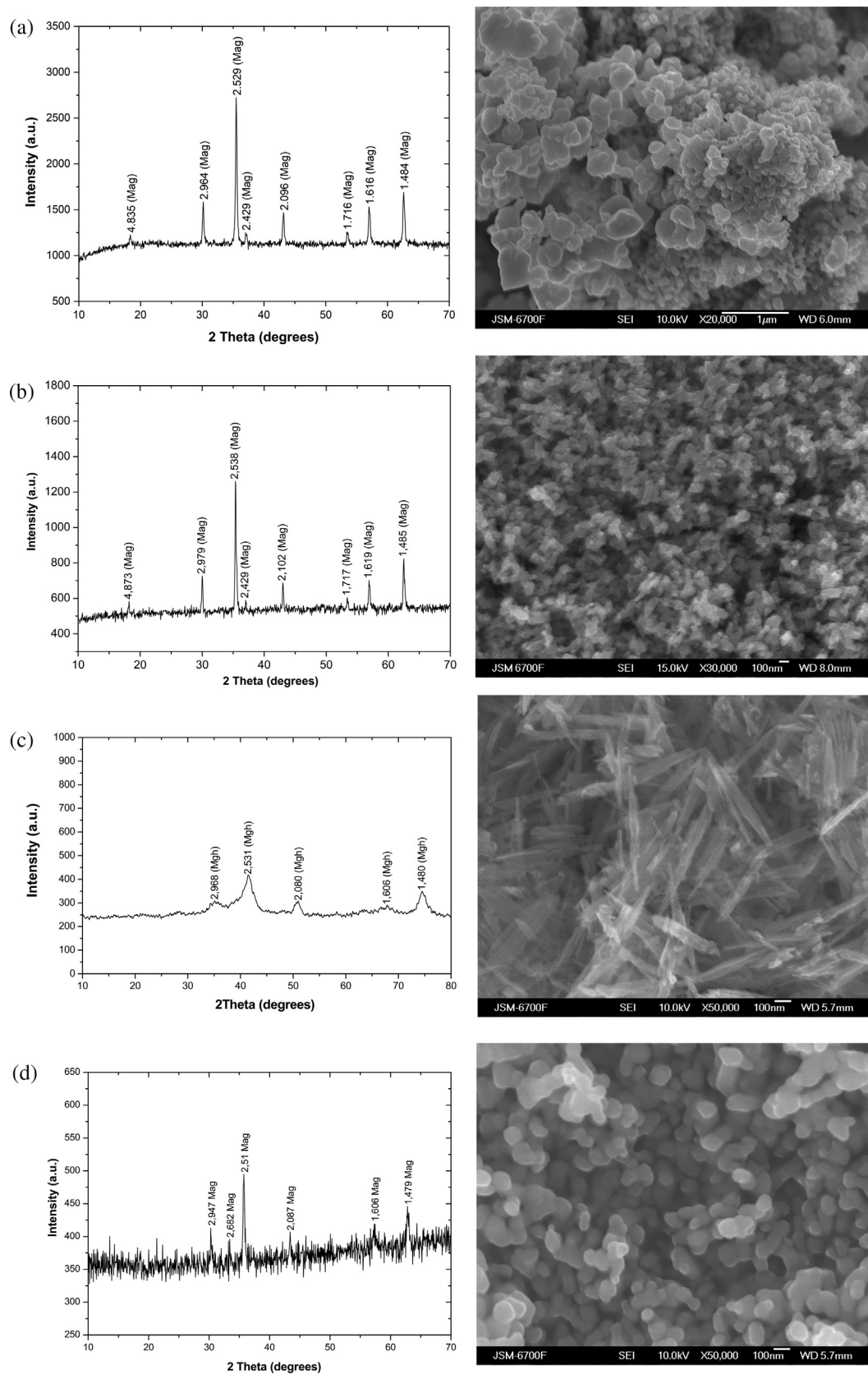


Fig. 6. XRD-patterns and SEM images of nanoparticles obtained from: (a) goethite ($T = 900\text{ }^{\circ}\text{C}$, $t = 10\text{ min}$), (b) hematite ($T = 900\text{ }^{\circ}\text{C}$, $t = 10\text{ min}$), (c) lepidocrocite ($T = 350\text{ }^{\circ}\text{C}$, $t = 10\text{ min}$, oxidizing conditions), (d) lepidocrocite ($T = 900\text{ }^{\circ}\text{C}$, $t = 10\text{ min}$, reducing conditions).

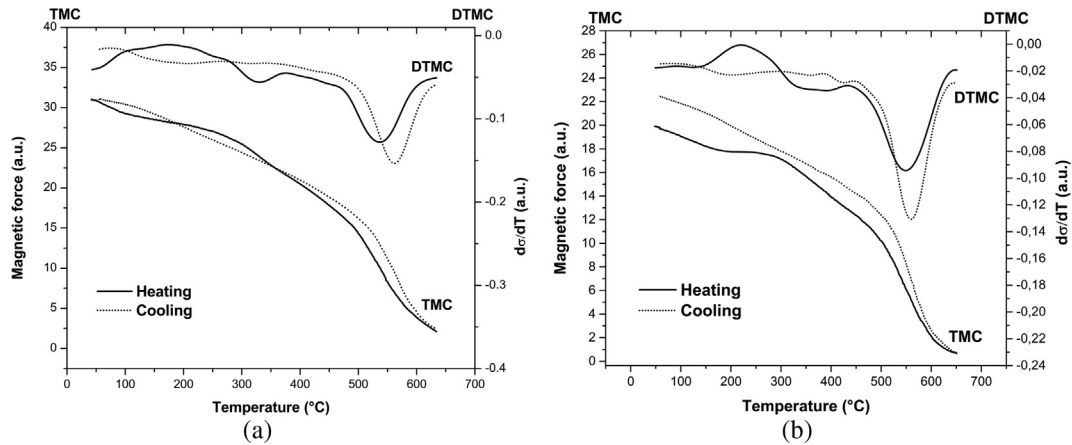


Fig. 7. Thermomagnetic analysis of the samples obtained by reduction of goethite (a) and hematite (b) at 900 °C for 10 min.

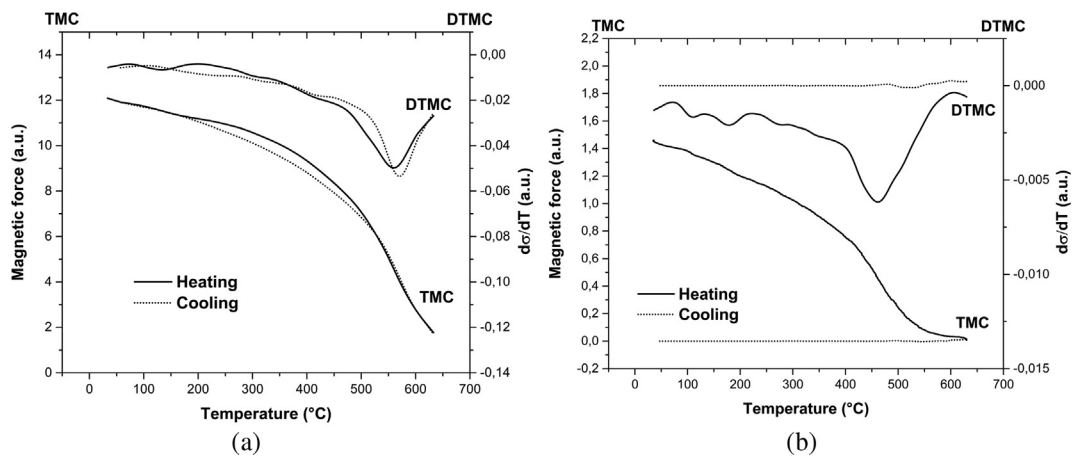


Fig. 8. Thermomagnetic analysis of transformed lepidocrocite nanoparticles under reducing (a) and oxidizing (b) conditions at 900 and 350 °C, respectively.

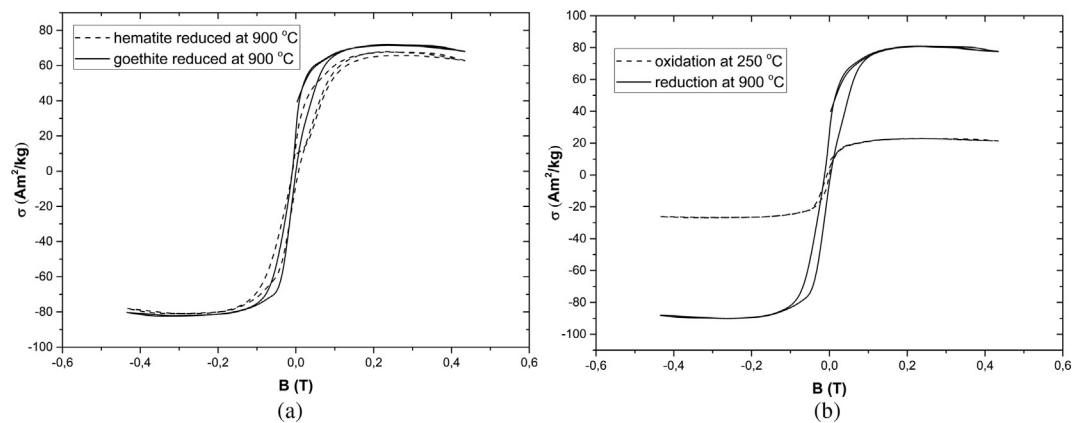


Fig. 9. Magnetization curves of transformed nanoparticles: (a) the reduction of hematite and goethite, (b) the reduction and oxidation of lepidocrocite.

Hematite. The conversion of hematite to magnetite under reducing conditions started at temperature of about 350 °C (Fig. 2). This correlates well with the literature data on experimental reduction of hematite. Ellid et al. [15] found that the starting temperature of magnetite formation by hematite reduction with starch is 300 °C. In our previous work [16], we showed that the reduction of synthetic and natural hematite by carbohydrates begun at approximately 350 °C and 365 °C, respectively. We have also found that

gaseous reduction of hematite ore in carbon monoxide atmosphere starts between 300 and 400 °C [26]. Thus, we can conclude that the hematite reduction starts at about 350 °C. The concentration and nature of a reducing agent, the origin of initial hematite and its particle size have a little effect on the starting temperature of the reduction. It should be noted that the higher reduction temperature of hematite with coal is a consequence of the high temperature of coal gasification (above 700 °C).

The conversion fraction of hematite to magnetite increased with temperature up to 700 °C (Fig. 2). At higher temperatures, there was a slight decrease in magnetization, which was associated with the partial oxidation of magnetite to hematite due to the combustion of the reducing agent. We did not observe this effect by studying the reduction of hematite in a continuous gaseous stream of CO and also found that complete transformation occurs at 500 °C [26]. A complete conversion of hematite to magnetite can be achieved even at 320 °C for reduction in H₂-Ar atmosphere [27]. Earlier, we have also observed that the conversion fraction of synthetic hematite is twice as high as for natural hematite particles [16]. Therefore, complete conversion of hematite to magnetite occurs over a wide temperature range, depending on the reducing agents, its concentration and the size of the hematite particles. In addition, it seems that the full conversion can be obtained at much lower temperatures if the reduction is carried out in a gaseous atmosphere rather than in the presence of carbohydrates.

The conversion fraction of hematite to magnetite by reduction with starch increased during the first 10 min of the reaction at 500 °C (Fig. 4). Extending time had little effect on further increasing the conversion fraction. This behavior is also characteristic of other temperatures in the range of 300–600 °C, as was shown using kinetic modeling [28]. By gaseous reduction in H₂-Ar, Gaviña et al. [27] obtained pure magnetite from hematite when heated for 40 min (T = 320 °C). We found the same optimal time for the reduction of natural hematite by carbon monoxide at 500 °C [26]. Hence, the time dependence of the conversion fraction of hematite to magnetite mainly depends on the origin of reducing agent.

The maximum saturation magnetization of magnetite obtained from hematite was almost 86 Am²/kg (Fig. 10), which is close to the typical value for pure magnetite (92 Am²/kg) [29]. It should be noted that the theoretical value of magnetite's magnetization is rarely achieved in practice, so even the obtained value for magnetite is the evidence of pure highly crystalline magnetite.

Goethite. Like hematite, goethite started to convert to magnetite at 350 °C (Fig. 2). However, a review of the literature data shows that the initial temperature of the formation of magnetite from goethite varies widely. Earlier, two different temperatures were

obtained for the conversion of goethite to magnetite – 260 °C for synthetic goethite and 500 °C for brown goethite ore [20]. According to Hanesch et al. [14], in the presence of 5–10 wt% of glucose, synthetic goethite is transformed into a highly magnetic mineral at 420 °C. Therefore, the temperature of transformation of goethite into magnetite varies for different samples. For natural samples, this may be explained by structural, textural, and chemical characteristics. However, the different reduction temperatures found for similar synthetic samples are still questionable. Note only the effect of the degree of crystallinity, which is also known to affect the temperature of the dehydroxylation of goethite [23].

Increasing the temperature from 300 to 900 °C led to an increase in the conversion fraction of goethite to magnetite due to the reduction with starch (Fig. 2). According to the literature, the complete conversion of goethite to magnetite can be achieved at different temperatures – 500–600 °C in [30], 700 °C in [20], and 800 °C in [31]. There appears to be a strong dependence of the reduction process on the mineralogy of original specimen and the nature of reducing agent. Therefore, the reduction kinetics of pure goethite is poorly studied and needs additional estimation.

Similar to hematite, the reduction of goethite with starch occurred mainly during the first 10 min of the reaction (Fig. 4). In the literature, different periods of reduction of goethite have been identified as optimal, depending on the mineralogy of initial samples and reducing agent. For example, the best magnetizing effect for limonite mixed with biomass was obtained when the roasting time was 30 min [32]. For reduction of goethite ore with pine sawdust, the optimal reaction time was 30 min [30].

The maximum saturation magnetization of magnetite obtained from goethite was approximately 88 Am²/kg, which is close to the theoretical value for magnetite.

Lepidocrocite. The starting temperature of thermal decomposition of lepidocrocite was 250 °C under both reducing and oxidizing conditions (Fig. 3). The data obtained are in good agreement with the literature review. A marked increase in magnetization was observed due to the formation of maghemite at about 200 °C [21] and 250 °C [22]. However, Gehring and Hofmeister [21] showed that superparamagnetic clusters of maghemite were formed even at 175 °C.

Since the values of magnetization of lepidocrocite transformed up to 350 °C are the same under both reducing and oxidizing conditions, it can be assumed that the formation of maghemite from lepidocrocite is responsible for increasing the magnetization over this temperature interval without the effect of a reducing agent. At temperatures above 350 °C, the influence of the reducing agent is obvious, leading to a marked increase in magnetization. We believe that this is due to the formation of magnetite via the reduction of hematite formed during the conversion of maghemite. On the contrast, Hanesch et al. [14] assume the formation of maghemite from lepidocrocite, which then transforms into weakly magnetic hematite under both reducing and oxidizing conditions.

Under oxidizing conditions, the thermal decomposition of lepidocrocite led to the formation of maghemite in the temperature range of 250–350 °C, whereas at 350–500 °C the newly formed maghemite was converted to hematite (Fig. 3). Similar results were reported in [21,22]. Under reducing conditions, the newly formed hematite is converted into magnetite, resulting in a dramatic increase in magnetization at temperatures up to 900 °C.

The effect of time on the treatment of lepidocrocite under reducing and oxidizing conditions is similar to that observed for hematite and goethite (Fig. 5). The reaction occurred in the first 10 min and then decelerated considerably. However, under oxidizing conditions, the magnetization continues to increase gradually with time. Cornell and Schwertmann [23] indicate that one of the methods for the synthesis of maghemite is based on heating

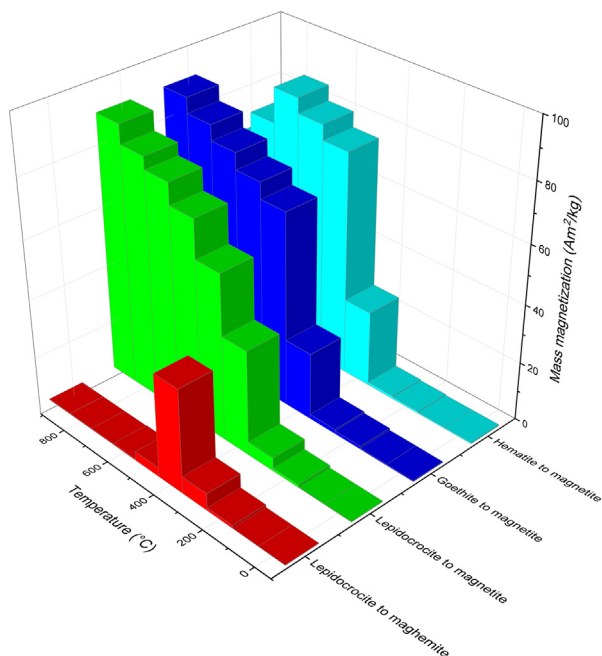


Fig. 10. Changes in saturation magnetization of initial iron oxide nanoparticles transformed under reducing and oxidizing conditions.

the lepidocrocite in air or in an oven at 250 °C for 2 h or 5 h, respectively. Therefore, annealing time seems important for the synthesis of maghemite from lepidocrocite, but it should be determined according to the selected temperature, for example, lower temperatures require more time for synthesis. The influence of time on the reduction of lepidocrocite is quite similar to that observed for synthetic goethite.

The maximum saturation magnetization was approximately 36 Am²/kg for maghemite obtained from lepidocrocite under oxidizing conditions and 88 Am²/kg for magnetite obtained from lepidocrocite under reducing conditions. The magnetization of the resulting magnetite is close to its theoretical value. The magnetization of maghemite is much lower than for nominal value of the saturation magnetization of maghemite – 74.3 Am²/kg [29]. However, several experimental works report similar values of magnetization – 34–39 Am²/kg [22] and 39.7 Am²/kg [33]. Gendler et al. [22] suggested that the low magnetization may have been caused by the fact that maghemite had already partially turned into hematite before all the lepidocrocite reacted. However, extremely small grain sizes and possibly poor crystallinity of maghemite can also reduce magnetization.

5. Conclusions

Changes in the magnetic properties of iron oxide nanoparticles, such as hematite, goethite, and lepidocrocite, have been studied by conventional heating under reducing and oxidizing conditions.

Thermal treatment of hematite and goethite in the presence of a reducing agent (5% starch) leads to their conversion into high magnetic magnetite. The starting temperature of transformation is about 350 °C for both samples. The morphology of the particles changes from acicular to isometric, with a variable diameter from tens to hundreds of nanometers. The magnetization is increased to 86 Am²/kg for hematite reduced at 700 °C and to 88 Am²/kg for goethite reduced at 900 °C. The intensive reaction occurs for the first 10 min, and then the conversion process decelerates significantly. The obtained Curie temperature of the samples corresponds to the value of pure magnetite.

Thermal treatment of lepidocrocite under both oxidizing and reducing conditions results in an increase in magnetization due to the formation of maghemite and magnetite, respectively. Regardless of the redox conditions, the formation of the magnetic phase begins at 250 °C and is associated with the formation of maghemite. However, at 350 °C the effect of the reducing agent becomes apparent. Under oxidation conditions, the magnetization decreases at 350 °C, which is associated with the formation of hematite. On the contrary, under reducing conditions, the magnetization increases up to 900 °C, which is associated with the formation of magnetite, most likely due to the reduction of the hematite formed from maghemite. The maximum values of magnetization are 36 Am²/kg for maghemite obtained at 350 °C and 88 Am²/kg for magnetite obtained at 900 °C. The flattened scales of lepidocrocite retain their morphology after conversion to maghemite and form spherical particles by reduction to magnetite.

Using conventional heating, the magnetic properties of IONs can be altered by phase transformations in the system FeOOH – Fe₂O₃ – Fe₃O₄. Temperature and redox conditions are two of the most important factors, controlling the transformation pathways and magnetic properties of the resulting samples.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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