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THERMAL TRANSFORMATION OF SYNTHETIC LEPIDOCROCITE BY DATA OF TERMEMAGNETOMETRY AND FERROMAGNETIC RESONANCE

The mechanisms of transformation of lepidocrocite (γ -FeOOH) heating under air remain unclear, regardless of numerical studies of thermal transformations of this mineral [1, 2, 3, 4]. Lepidocrocite is lower spread in nature, then goethite (α -FeOOH). The orthorhombic structure of lepidocrocite is formed by the hexagonal layers of O^{2-}/OH^- anions, stacked in the [150] direction, H^+ ions are located along the line between of two O^{2-} ions ($O - H \cdots O$), and Fe^{3+} ions occupy octahedral sites [2, 3]. Heating of lepidocrocite under air results, like goethite, in structure dehydroxylation – destruction of OH groups and remove of formed H_2O molecules from the structure [1, 2, 4]. Dehydroxylation of γ -FeOOH, unlike α -FeOOH, occurs in some stages [3]. Initially weakly bound molecular water desorbs, then dehydroxylation results in forming of maghemite ($2(\gamma\text{-FeOOH}) \rightarrow \gamma\text{-Fe}_2\text{O}_3 + H_2O$), which transforms to hematite ($\gamma\text{-Fe}_2\text{O}_3 \rightarrow \alpha\text{-Fe}_2\text{O}_3$) [2, 3]. Maghemite ($\gamma\text{-Fe}_2\text{O}_3$) forms at lower temperatures, $T \approx 200 - 300$ °C, and transform to hematite, $\alpha\text{-Fe}_2\text{O}_3$ (hexagonal structure), at the temperatures from 350 to 600 °C [1, 2, 4]. The [150] direction of the orthorhombic unit cell corresponds to the [111] direction of a distorted cubic cell, that facilitates lepidocrocite dehydroxylation to the spinel phase – maghemite (Mgh) [2]. The dehydroxylation of lepidocrocite results in forming of aggregations of nanocrystals (≈ 10 nm) of the cubic maghemite with the disordered distribution of iron vacancies (V_{Fe}) [2]. Heating of the cubic maghemite can result to enlarge of crystallites and forming of the tetragonal maghemite (Mgh2) with the ordered V_{Fe} distribution and the relation of $c/a \approx 3$ for the lattice parameters [2]. These changes lead to significant changes in the properties, in particularly, to decrease in the Curie temperature from $T_C \approx 650$ to 580 °C ($\approx T_C$ of magnetite). Lepidocrocite can transform to hematite (Hem) when dehydroxylation occurs very slowly [2].

The aim of the present work was to synthesize of lepidocrocite from the aqueous solution of iron (II) sulfate and to identify of iron oxides formed during the thermal conversion of lepidocrocite using by structural and magnetic methods. Lepidocrocite (Lps) was synthesized by low-temperature precipitation from the aqueous solution and divided into some samples. Some of the obtained samples were heated isothermally at temperatures $T = 250 - 550$ °C and $T = 100 - 800$ °C with the 100 °C step exposing for 20 and 60 min at each temperature, respectively. The samples were studied using methods of X-ray phase analysis (XRD), thermomagnetometry (TMA) and ferromagnetic resonance (FMR). Diffractograms were obtained by the standard methodic using DRON 3M. TMA was performed using the device for measuring the Curie temperature [5] at a heating velocity of 60°/min up to 350 °C, espousing during 5 and 10 min at this temperature and cooling with the same velocity. The saturation magnetization ($M_s(T)$) and the first derivate, dM_s/dT (differential thermomagnetic curve (DTMC)) in the magnetic field of 350 mT in dependence on the temperature were recorded. FMR spectra were recorded on LEXIS-580 spectrometer (Bruker, X-band).

A batch of lepidocrocite was synthesized in the following way, analogously by [3]. There were prepared of 300 ml water solution of iron (II) sulfate, dissolving 16.68 g of $FeSO_4 \cdot 7H_2O$ in water, and 1 M NaOH, dissolving 7 g of NaOH in 250 ml of water. 1M NaOH was added to the iron (II) sulfate solution until pH = 6.7 - 6.9 was approached (the pH value needed for lepidocrocite precipitation), until the dark green color of the solution was obtained. The suspension was aerated with continuous magnetic stirring. The pH and temperature of the suspension were recorded. A small amount of 1M NaOH was added to adjust pH = 6.7 – 6.9, until the suspension color changed to yellow-orange. After the reaction was completed, the precipitate was removed from the suspension and washed with water (50 ml) by centrifuging and dried in a thermostat until an unchanged weight was approached.

XRD showed the following main reflexes of the precipitate: 0.618; 0.328; 0.246 and 0.193 nm. Such values practically correspond to the standard reflexes of lepidocrocite [3]. Heating of Lps for 20 minutes at $T = 250$ and 350 °C resulted in forming of the X-ray amorphous phase, which transformed into the crystalline hematite at $T = 450$ and 550 °C, respectively.

TMA showed the following. When the sample was heating the magnetization M_s increased at 200 °C, to the extremum at 280 °C and, after a break, to 350 °C. The exposure for 5 min as this temperature was resulted in the slightly decrease of M_s . The cooling curve demonstrated the ferromagnetic (FM) phase with the Curie temperature of $T_C = 335$ °C and the M_s increase in ≈ 2 times. The magnetization has increased in ≈ 3.5 times, relative to Lps, after the heating/cooling cycle. When the sample was heating TMA with the exposure for 10 min at $T = 350$ °C showed (Figure 1, a) the extremes of M_s increase: insignificant – at ≈ 220 °C and two main – at 290 and 350 °C, with approximately the same contribution to magnetization. The value

of M_s increased by more than an order of magnitude during sample heating, did not change practically during 10 min and continued to increase when the sample was cooling. The value of M_s was been in ≈ 20 times larger, then Lps (the original sample), after cooling. The cooling curve showed appearance of FM phases with $T_C = 310$ °C (main) and additional phases with ≈ 260 and 200 °C (Figure 1, a).

FM phases were absent up to 350 °C when the heating/cooling velocity was $20^\circ/\text{min}$ without stopping up to 650 °C. The magnetization M_s at this temperature (350 °C) dropped almost to zero. This shows that the heating velocity was low, so the FM phases were forming during the dehydroxylation of lepidocrocite and transformed quickly to hematite.

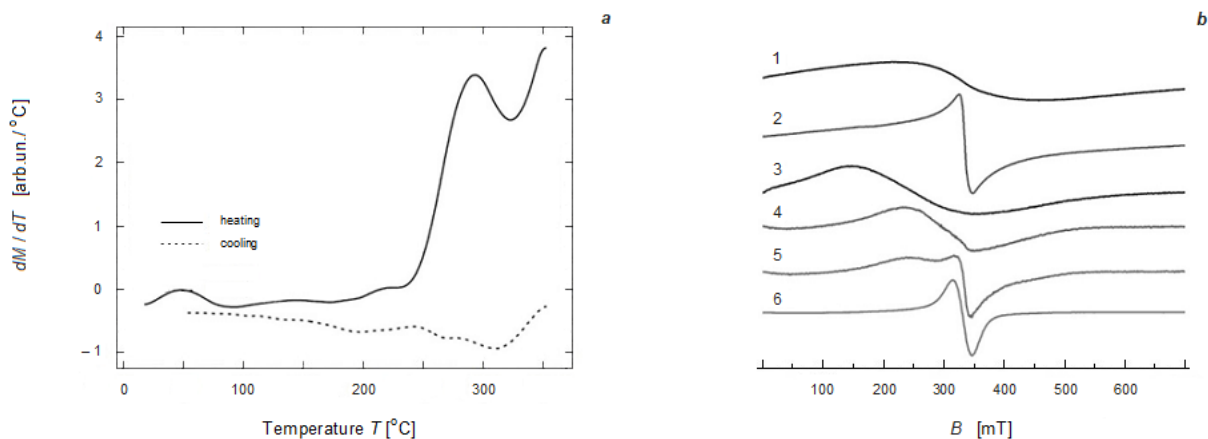


Fig. 1. The study of lepidocrocite Lps: (a) DTMA, (b) FMR spectra (the first derivative of the signal) of the synthesized Lps (1) and after isothermal heat at T (°C) = 200 (2), 500 (3), 600 (4), 700 (5) and 800 (6)

FMR allows establish FM phases [6, 7]. In particularly, the parameters B_1 , B_{res} and ΔB of the cubic and tetragonal maghemite ($\gamma\text{-Fe}_2\text{O}_3$) are 270, 300, 80 and 220, 290, 210 mT, respectively [6]. Thus, these maghemites differ significantly by the parameters B_1 and ΔB of FMR signals.

The FMR spectrum (Figure 1, b, Table 1) of the synthesized Lps is presented by the broad band on the resonance magnetic field of $B_{\text{res}} \approx 300$ mT with the width of $\Delta B = 237$ mT (curve 1). To clarify the structures of FM phases formed during thermolysis of lepidocrocite, the samples were heated isothermally to 800 °C (with the exposure of 60 min at each temperature).

Table 1. Parameters B_{res} , B_1 , B_2 and ΔB and intensity (I) of the FMR spectra of the synthesized lepidocrocite and one after isothermal heat at the listed temperatures

Parameter	Temperature, °C								
	20	100	200	300	400	500	600	700	800
B_{res} [mT]	300	305	305	270	260	255	280	300	305
B_1 [mT]	166	155	295	260	220	270	250	290	294
B_2 [mT]	413	410	320	390	430	350	360	315	326
ΔB [mT]	237	245	25	106	137	207	117	25	32
I [rel. un.]	0.00	0.02	0.04	1.00	0.90	0.52	0.02	0.01	0.02

Note. Parameters of the first derivative of the FMR signal: B_{res} – the resonance magnetic field, B_1 and B_2 – extremums, $\Delta B = B_2 - B_1$ – the line width

The FMR signal was narrowed substantially with the intensity increase for the sample heated to 200 °C, in addition, the very narrow band was appeared at $\approx B_{\text{res}}$, nearly an order of magnitude smaller in width (curve 2). Heating of Lps up for 300 °C led to (Table 1) the intensity increase, the shift to lower magnetic field and the significant broadening of the FMR signal. After heating at 400 and 500 °C (curve 3), the intensity of the signal gradually decreases with the band broadening. Heating of Lps at 600 °C (curve 4) resulted in the shift of the band to the higher magnetic field and division of the signal into two components – wide component ($\Delta B \approx 150$, $B_{\text{res}} \approx 260$ mT) and narrow one ($\Delta B \approx 26$, $B_{\text{res}} \approx 300$ mT). After heating of Lps at 700 °C (curve 5) and 800 °C (curve 6), the narrow component intensity increased gradually, but the wide component intensity dropped at 700 °C. This component was absent after heating of Lps at 800 °C.

The narrow component for Lps heated up to 200 °C and the narrower component for the sample heated at $T \geq 600$ °C are due to hematite, based on the spectrum parameters [7]. FMR spectrum of Lps heated at $T \leq 200$ °C shows the mixture of amorphous phase and hematite, at $T = 500$ °C – maghemite [6], the component of Hem, moreover, does not appear due to its low intensity. The FMR signals of Lps heated at $T = 600$ and 700 °C are due to Mgh and Hem.

The comparison of the obtained TMA and FMR data shows that quickly heating of lepidocrocite to 200 °C does not lead to significant changes in its magnetic structure, but hematite forms during slow heating. When Lps was heated slowly to 300 °C, the FM phase formed at $T \approx 280$ °C. The FMR spectrum of this sample after cooling showed appearance of mixture of maghemites differed in structures, most likely, as a result of enlarged of some crystallites. TMA up to 350 °C with the exposure for 5 min showed the formation of the FM phase with the Curie temperature of $T_C = 310$ °C. The cooling curve clearly demonstrated it for the exposure for 10 min (Figure 1, a). This Curie point is significantly lower than that of cubic maghemite ($T_C = 650$ °C) and tetragonal maghemite ($T_C \approx 580$ °C $\approx T_C$ of magnetite) [2]. This can indicate to Na impurities and the presence of V_{Fe} in tetrahedral sites, which results in significantly reduces of the T_C of maghemite [2].

FMR spectrum of the sample heated at 300 °C (Table) is caused by the cubic maghemite (Mgh1) with the tetragonal one (Mgh2) impurity based on the signal parameters. Content of Mgh2 increases significantly when the temperature of isothermal heating elevates to 400 and 500 °C. The ratios of the contents of different types of maghemites in samples heated in this temperature range are following: $Mgh1 > Mgh2$, $Mgh1 \geq Mgh2$ and $Mgh1 < Mgh2$, respectively. The broadening of the FMR signal and its shifts to lower magnetic field (Figure, b, Table) indicates increase of Mgh2 content. Thus, elevate in the temperature of isothermal heating leads to enlarge of Mgh1 crystals and formation of the Mgh2 structure. Most of the Mgh2 phase is transformed to hematite during Lps heating at $T = 600$ °C. The rest part of this phase remains after heating at 700 °C. Therefore, the inversion temperature to hematite of the phase Mgh1 formed during the dehydroxylation of synthesized Lps and, possibly, containing the Na impurities, is $T_{inv} \approx 800$ °C. This value lies within the range of the inversion temperatures of maghemites of different genesis and origin [2].

Heating of lepidocrocite at 500 °C in the presence of starch (4%) led to quick dehydroxylation and partial reduction of the structure to magnetite. Lps heating for 5 min at these condition resulted in formation of the solid solution of Mgh in magnetite (Mag) with the Curie point of $T_C = 570$ °C and phase contents of $Mag > Mgh$ by FMR data. The exposure for 20 min at this temperature resulted in formation of the FM phase with $T_C = 632$ °C, close to tetragonal maghemite (Mgh2) by FMR data.

The present study showed the effectiveness of using of the complex of magnetic methods, thermomagnetometry and FMR, for the identification of ferromagnetic (FM) phases formed during the thermal transformation of synthetic lepidocrocite. It was established that Lps heating up to 280 and 350 °C resulted in formation of two FM phases, the cubic (Mgh1) and tetragonal (Mgh2) maghemites, respectively. The Mgh1 phase is thermally unstable and transforms into hematite. The thermal stability of the Mgh2 phase, which structure close to tetragonal maghemite, possibly, with Na impurities and tetragonal iron vacancies, and the Curie point of $T_C = 310$ °C, is substantially higher: the inversion temperature to hematite is ≈ 800 °C. The comparison of TMA and FMR data shows that the lepidocrocite heating at 500 °C in the presence of starch (4%) leads to the rapid (for 5 min) partial reduction of the structure to magnetite, and the exposure for 20 min at $T = 570$ °C results in formation of the FM phase closed to tetragonal Mgh2. The obtained results can be used to identify maghemite in iron quartzites during their preparation before enrichment.

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