



CHEMICAL SCIENCES

New insights on the Jacobsite mineral from Bahia and related synthetic manganese-ferrite nanoparticles

LUCAS F. QUARTAROLLI, FERNANDO M. DE MELO, JOANIEL M. MARTINS, ALCEU T. SILVEIRA-JUNIOR, MARCELO NAKAMURA & HENRIQUE E. TOMA

Abstract: Jacobsite is a relatively rare mineral of composition MnFe_2O_4 , found in Urandi (Bahia State) in Brazil. It is also a common species in the deep-sea manganese nodules, attracting the interest of many mineral-extracting companies. Because of its spinel constitution similar to magnetite, Jacobsite is commonly called a manganese-ferrite. However, the manganese/iron content may vary substantially according to its origin, demanding specific studies in each case. The Jacobsite mineral inspired our laboratory synthesis of the analogous manganese ferrite nanoparticles. The direct synthesis by the coprecipitation method has not been successful; however, it can be carried in the presence of citrate ions, yielding strongly magnetic nanoparticles, with a maximum magnetization of 45.6 emu.g^{-1} . Although they were structurally identical to Jacobsite, the mineral from Bahia exhibited a rather weak magnetism, because it involves a ferrimagnetic coupling. For this reason, the synthetic method seems to provide a better way of obtaining strongly magnetic manganese ferrites. These magnetic nanoparticles have been investigated in detail, including their interaction with diatoms, providing interesting magnetic bio-silicate carriers in drug delivery.

Key words: Jacobsite mineral, manganese ferrites, iron-manganese oxides, magnetic oxides, magnetic nanoparticles, X-ray diffraction.

INTRODUCTION

Jacobsite is a natural manganese iron oxide of composition MnFe_2O_4 , belonging to the spinel group where the Mn(II) ions occupy the tetrahedral sites and the Fe(III) ions are present in octahedral sites. Its name derives from Jacobsberg, where it was discovered in Sweden. Although relatively rare, it can be found in countries such as Namibia, South Africa, India, Australia, Japan, and Brazil, exhibiting variable composition from the partial exchange of Mn(II) by Mg(II) or Fe(II) ions. Because of its great similarity with magnetite, Fe_3O_4 , Jacobsite is often referred to as manganese ferrite.

In Brazil, the mineral can be found in Pacatuba (Ceara State) and Urandi (Bahia State) (Ribeiro Filho & Marinho 1983), from which a well-formed sample (Figure 1) has been obtained and investigated in this work. Considering the variable composition of Jacobsite, mineral characterization is necessary for a better understanding of its properties and structure.

On the other hand, it should be noted that Jacobsite is also an important component of the so-called manganese nodules that grow in deep-sea bottoms (Timofeeva et al. 2014, Exon et al. 2002). Such nodules exhibit a high metal content and are currently attracting the interest of many mineral-extracting companies. Their genesis is yet a subject of debate (Benites et

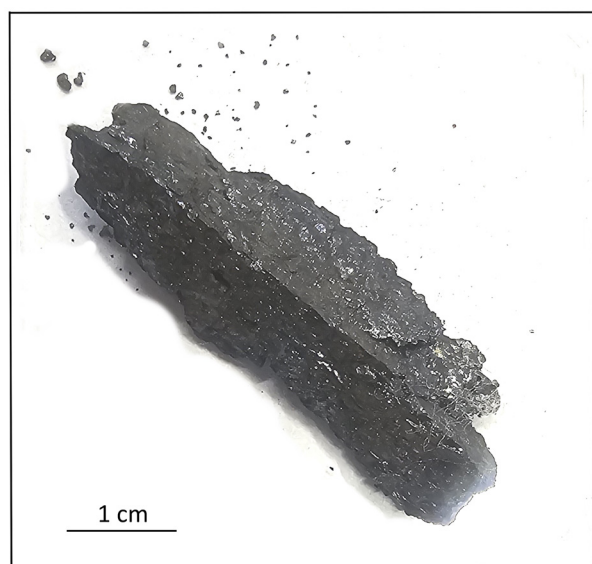


Figure 1. Jacobsite mineral sample from Urandi mines (Bahia State, Brazil).

al. 2018) and seems to involve the precipitation of the iron and manganese oxides from oxic seawater, at a rate of a few mm per million years, according to a hydrogenetic pathway. The genesis can also involve the generation from sediments (diagenetic), in addition to the biogenetic pathways (Hassan et al. 2020).

The Jacobsite mineral has inspired our laboratory work on synthetic manganese ferrites, MnFe_2O_4 . In the literature, their synthesis has been performed on the macro-scale, based on coprecipitation methods coupled with high-temperature annealing (Tariq et al. 2015, Dong et al. 2013, Jiao 2011).

Nowadays, there is a great interest in synthetic manganese ferrites in the nanoscale, because they can be useful in electronic, magnetic, and chemical processes, as well as in magnetic resonance imaging (Jiao 2011). However, our initial attempts to generate the MnFe_2O_4 nanoparticles using the classical coprecipitation method were not successful, yielding a non-magnetic material. After many attempts, through factorial planning, high-quality superparamagnetic MnFe_2O_4 nanoparticles have

been obtained using citrate as a stabilizing agent, in an aqueous solution. Because of its relevance, the synthesis and characterization of such manganese ferrite nanoparticles are reported in this paper, including their interaction with diatom carriers, aiming for possible applications in drug delivery. In addition, a comparison of the Brazilian Jacobsite mineral and the manganese ferrite nanoparticles has also been performed, providing important clues on their magnetic properties and contrasts from the macroscopic and nanometric scales.

MATERIALS AND METHODS

Chemicals

All reagents and solvents were purchased from Sigma Aldrich and used without previous purification. Diatoms can be obtained from inexpensive sources such as diatomaceous earth, after a careful fractionation as reported in the literature (Losic et al. 2010). In this work, commercial diatomaceous earth was suspended in water and three fractions were collected along the decantation process, corresponding to fine, medium, and large particles. The several samples were monitored with an optical microscope, and the medium-size fraction was selected in this work, aiming to find nearly intact diatom shells for interacting with the magnetic nanoparticles. The fine fraction was plenty of small shell fragments, while the large ones exhibited all kinds of diatom structures deposited at the bottom of the flask.

Synthesis

The manganese ferrite was synthesized by the following co-precipitation method: In a round-bottomed flask, 50 mL of a 2 M solution of NaOH was stirred under a nitrogen flow and mixed with 25 mL of a previously prepared solution containing 0.127 g of $\text{MnCl}_2 \cdot \text{H}_2\text{O}$ and 0.347 g of

FeCl₃ and with 5 mL of a citric acid solution (1 M) under stirring at 1200 RPM, for 10 min. The initial yellow solution turns immediately black. After this step, the mixture was heated under reflux for 60 min, forming a fine black precipitate. After cooling to room temperature, the solid was separated using a neodymium magnet (Nd₂Fe₁₄B), and washed three times with water, then with ethanol and acetone. The final drying was performed at 80 °C in an oven.

Measurements

Visible-UV Spectra were obtained with an Agilent HP-8453 diode-array spectrophotometer, in the range of 190-1100 nm. Dynamic light scattering (DLS) and Zeta potential measurements were carried out with Malvern Zetasizer Nanorange equipment. Thermal analysis (TGA, DTA) was performed using Shimadzu DTG 60 equipment, working under an air atmosphere. Infrared spectra were obtained with an Alpha Bruker spectrophotometer in the range of 360 – 4000 cm⁻¹. X-ray diffractograms (XRD) were recorded using a Bruker D2 Phaser spectrometer, scanning in the range of 2θ from 7° to 90°, using Copper Kα irradiation (λ = 1.5408 Å), at 30 kV and 14 mA power, with an SDD detector working at -20 °C. X-Ray fluorescence spectra were collected with a Shimadzu, EDX-720 spectrometer with a rhodium source operating at 5-50 kV and 1-1000 μA, and a Si(Li) detector. Raman spectra and images were obtained with a Witec Alpha 300R confocal microscope, operating at 488, 532, and 633 nm, with CCD and EMCCD detectors. Hyperspectral images were obtained with a CytoViva dark-field microscope with the samples placed on ultraclean Nexterion, Schott glasses. Atomic force microscopy (AFM) images were obtained with a Bruker Multimode VIII Nanoscope IIIA instrument, using the magnetic force mode. Magnetic measurements and hysteresis curves were obtained using a vibrating sample

magnetometer (VSM) manufactured by EG&G Princeton Applied Research – model 4500.

RESULTS AND DISCUSSION

The synthesis of manganese-ferrite nanoparticles was achieved in high yield by the coprecipitation method using citrate ions as stabilizing agents. The strong nanoparticles magnetism gave good evidence of success. By performing the regular synthesis using coprecipitation methods, non-magnetic particles were obtained. For this reason, most methods in the literature apply thermal treatment or annealing at very high temperatures, to convert the solids into crystalline MnFe₂O₄ (Jiao 2011). However, in this case, despite their relatively strong magnetism, the nanoscopic properties are lost.

In this work, the study of the manganese-ferrite nanoparticles was performed in comparison with the Jacobsite mineral from Bahia, to appreciate the differences between the macro and nanoscale. The investigation was carried out using EDX, XRD, FTIR, Raman, VSM, TGA, DTA, CytoViva, DLS, and Zeta potential techniques.

EDX analysis

The composition of the synthetic manganese-ferrite nanoparticles was probed by energy-dispersed X-ray fluorescence (EDX), as shown in Figure 2. The results obtained with Jacobsite were also included for comparison purposes. In both cases, the dominant peaks correspond to iron (Fe Kα) and manganese (Mn Kα) emissions, in the 2:1 proportion, as expected by the MnFe₂O₄ composition. In the expanded scale, it is possible to detect trace amounts of Al, Si, S, Cl, K, and Ca, especially in the Jacobsite mineral. In comparison with the manganese-ferrite nanoparticles, about a 10% reduction in the intensity of the Fe and Mn peaks was

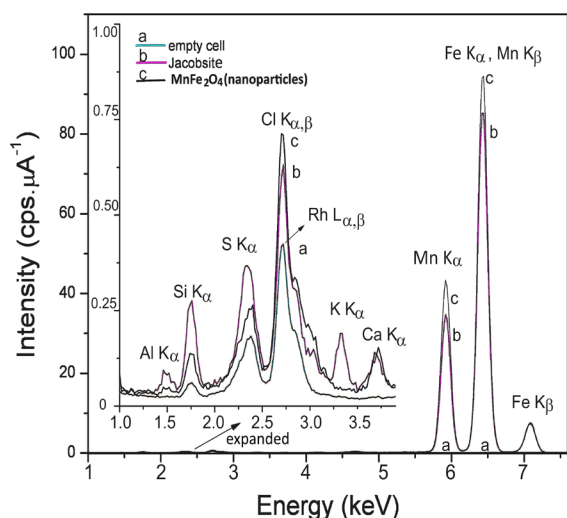


Figure 2. EDX spectra of Jacobsite and the synthetic MnFe_2O_4 nanoparticles, showing the predominance of the Fe and Mn peaks, in the 2:1 proportion, and traces of the Al, Si, S, Cl, K, and Ca, contaminants shown in the inset (100 × expansion).

observed for Jacobsite, implying the existence of light element contaminants, such as Mg, not detected by the EDX instrument.

X-Ray Powder diffraction

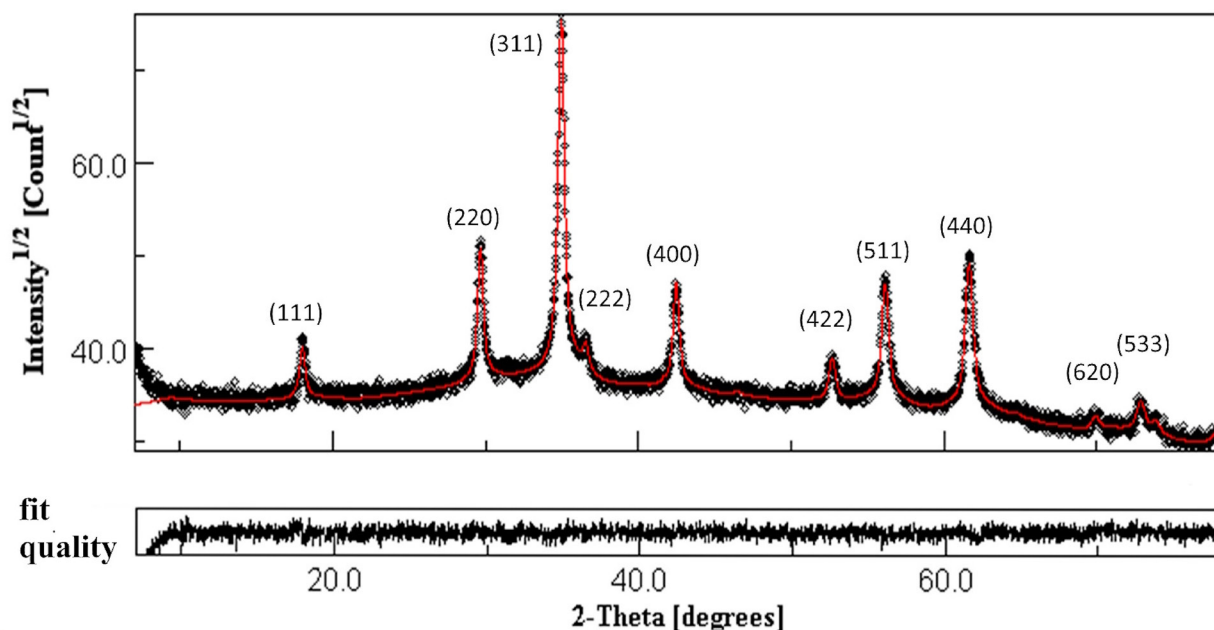


Figure 3. DRX plots for the synthetic manganese-ferrite nanoparticles (black) and theoretical simulation (red) based on Rietveld analysis.

The X-ray powder diffractograms of Jacobsite and manganese ferrite nanoparticles can be seen in Figures 3 and 4. Jacobsite and the manganese ferrite exhibit rather similar XRD patterns, consistent with a cubic, $Fd3m$ space group, with $a = 8.506 \text{ \AA}$, in excellent agreement with the literature. (Jacobsite Mineral Data, <https://webmineral.com/data/Jacobsite.shtml> n.d.) reference number 74-2403 from JCPDS International Centre for Diffraction Data.⁷⁴

Rietveld simulations (Rietveld 1969) for the manganese ferrite nanoparticles lead to consistent results, reproducing the XRD pattern with high accuracy, as shown in Figure 3.

From the Rietveld calculations, the average particle size was 32.89 nm, compared with 30.19 and 21.49 nm, based on the Williamson-Hall and Scherrer formalisms (Borbély 2022). The radii of the tetrahedral and octahedral sites were calculated as 0.580 and 0.772 Å , respectively. The MnFe_2O_4 content was 94.6%, and magnetite Fe_3O_4 appears as a contaminant at about 4.64%. The remaining impurities did not exceed 0.75%.

In the case of Jacobsite, the experimental diffractogram (Figure 4) was very similar to that obtained for the synthetic manganese-ferrite nanoparticles; however, the observed peaks are much narrower and typical of crystalline material. The observed broadening in the case of the synthetic manganese-ferrite species (Figure 3) is consistent with their nanometric dimension. In Figure 4, the minor peaks observed

for Jacobsite at $2\theta = 25.853^\circ$ and 69.317° are due to impurities from the mines.

Thermal analysis

The thermal analysis (TGA and DTA) of the synthetic manganese-ferrite nanoparticles and Jacobsite mineral can be seen in Figure 5a and b, respectively. In the case of the manganese-ferrite, heating up to 132 C leads to a mass loss

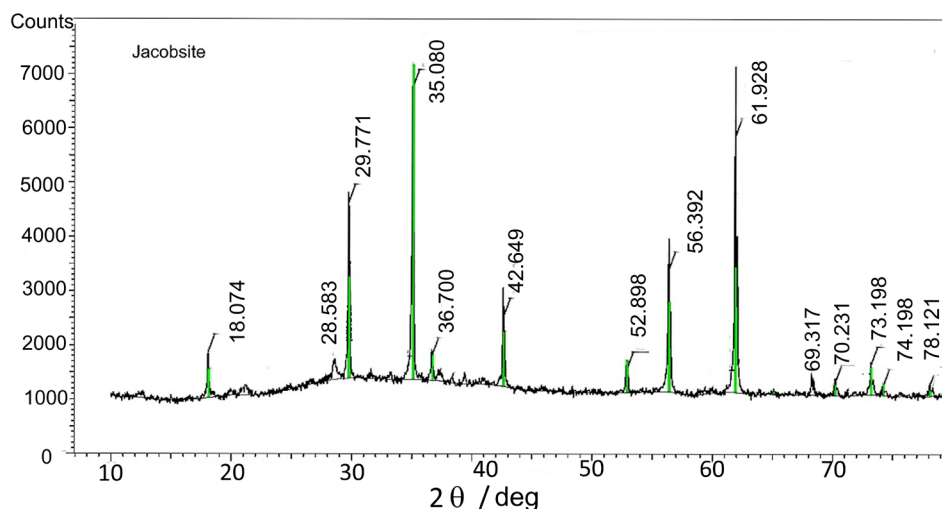


Figure 4. Powder diffractogram of Jacobsite (from Bahia, Brazil) superimposed to the literature data (green).

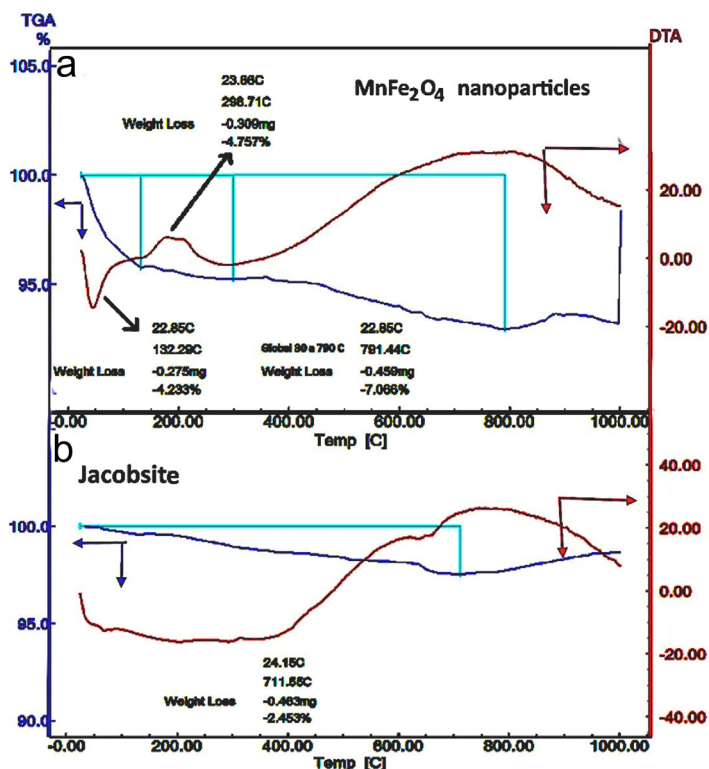


Figure 5. Thermal analysis (TGA and DTA) of (a) synthetic manganese-ferrite nanoparticles and (b) mineral Jacobsite, under a normal atmosphere.

of 4.2 %, and the observed endothermic process can be associated with the removal of the water molecules from the nanoparticles. Around 200 °C there is an exothermic peak with a loss of mass of 0.5 %, consistent with the burning of the citrate coating on the particles. Above 400 °C, there is a broad exothermic peak accompanied by a 2 % loss of mass. This thermal behavior is also observed in Jacobsite (Figure 5b), indicating chemical transformations in the MnFe_2O_4 material, promoted by the high temperatures.

Dynamic light scattering and Zeta potentials

An interesting point is that the synthetic manganese ferrites can be redispersed in water through a mild ultrasonic stirring, allowing the monitoring by dynamic light scattering and Zeta potentials, as shown in Figure 6a and b.

The DLS measurements showed a monomodal distribution of nanoparticles (pdi =

0.294) of about 70 nm in aqueous solution, with Zeta potential of -13.3 mV imparted by the citrate ligands at the surface. Because of the relatively small Zeta potentials, the nanoparticles were not particularly stable in aqueous solution, leading to slow successive changes in the light scattering behavior (Figure 6) due to aggregation. On the other hand, the observed hydrodynamic radii, as compared with the XRD measurement, are consistent with aggregation of the nanoparticles after the sonication process.

FTIR and Raman spectra

The vibrational spectra of the manganese ferrites can be compared with those of the isomorphous magnetite (Fe_3O_4) nanoparticles. It should be noted that magnetite exhibits 5 active vibrational modes in the Raman spectra, of symmetry A_{1g} , E_g , and $3 \times T_{2g}$. The major band occurs at 670 cm^{-1} corresponding to the A_{1g} mode (Shebanova &

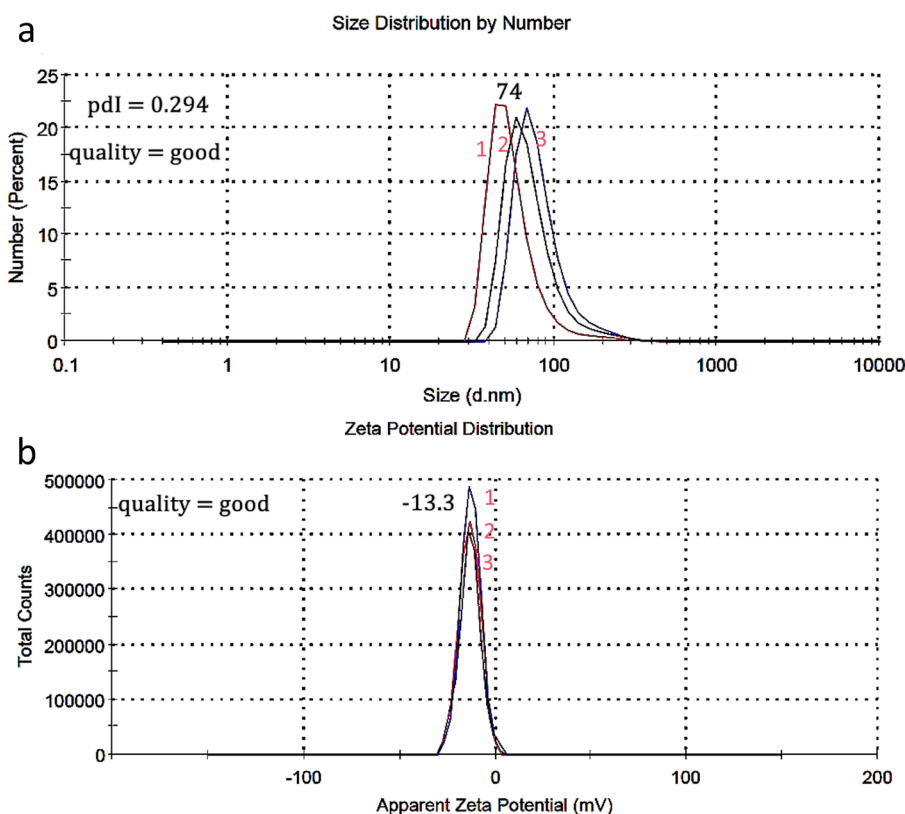


Figure 6. Dynamic light scattering curves (a) and Zeta potentials (b) for the synthetic manganese-ferrite nanoparticles; showing triplicate measurements represented by curves 1-3, with the small changes promoted by their aggregation tendency in aqueous solution.

Lazor 2003). In addition, there are four infrared active vibrational modes, corresponding to T_{1u} symmetry. The strongest band occurs at 580 cm^{-1} . Because of the cubic system, there is an inversion center in the crystal, and the Raman and infrared transitions involve a mutually exclusionary regime.

The FTIR spectra of the manganese-ferrite nanoparticles and Jacobsite can be seen in Figure 7.

The most relevant peaks in manganese-ferrite are observed at 583 cm^{-1} corresponding to the metal-oxygen stretching vibration of T_{1u} symmetry. This band is shifted to 552 cm^{-1} in the case of Jacobsite, presumably because of the

lattice influences from the crystal. Evidence of the citrate ligand can be seen at 1570 and 1350 cm^{-1} , corresponding to the symmetric and anti-symmetric vibrations of the carboxylate groups. These signals are not observed in the Jacobsite spectra. The strong bands around 3400 e 1600 cm^{-1} arise from residual water molecules in the samples, as well as in the KBr pellets. Jacobsite also exhibits additional peaks, of low intensity, around 1000 cm^{-1} consistent with Si-O vibrations from silicate impurities, as detected in the EDX spectra.

The corresponding Raman spectra, recorded from the same KBr pellets employed in the FTIR measurements, are shown in Figure 8.

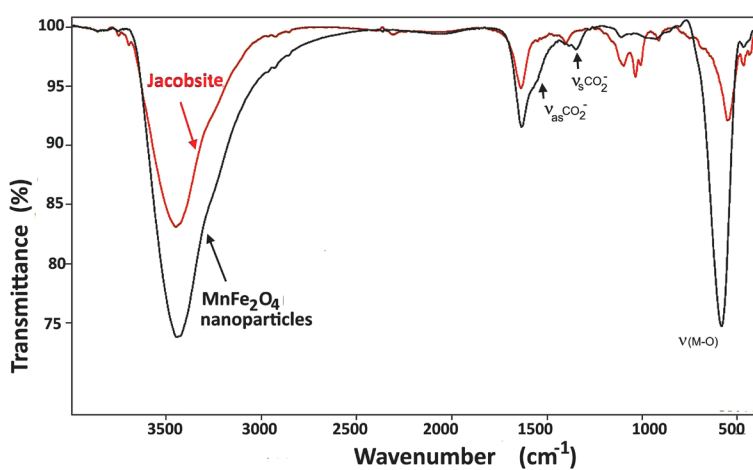


Figure 7. FTIR spectra of the manganese-ferrite nanoparticles and Jacobsite, recorded in KBr pellets.

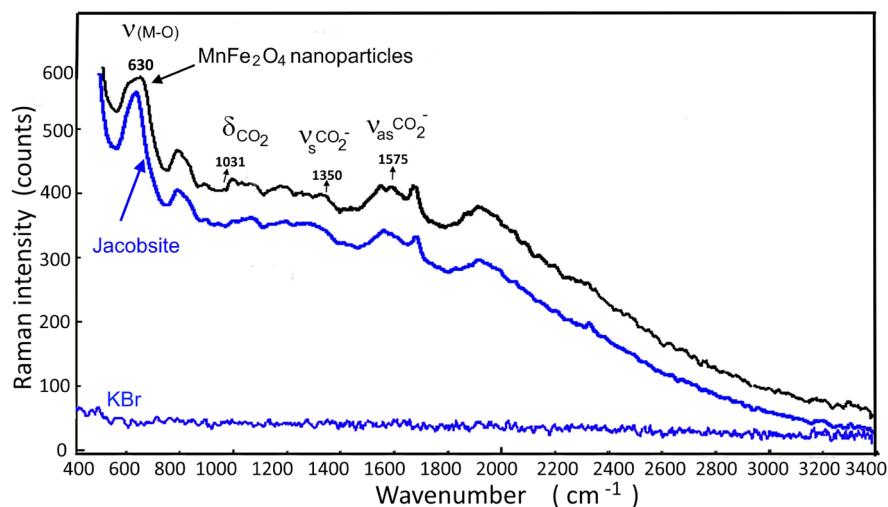


Figure 8. Raman spectra of the synthetic manganese-ferrite nanoparticles and Jacobsite, recorded from the KBr pellets employed in the FTIR measurements.

In the case of the manganese-ferrite nanoparticles, the strongest peak in the Raman spectra is observed at 630 cm^{-1} corresponding to the expected A_{1g} vibrational transition observed at 670 cm^{-1} in magnetite. The shape of the asymmetric peak may be due to the small amount of magnetite (4.6%) present in the sample. Evidence of citrate ions can be seen at 1031 , 1350 , and 1575 cm^{-1} corresponding to the expected vibrations of the carboxylate groups (Nakamoto 1986). Jacobsite exhibits a major Raman peak at 630 cm^{-1} , corroborating the results observed for the manganese-ferrite nanoparticles.

Magnetic properties

A differential aspect of the synthetic manganese-ferrite nanoparticles, as compared with Jacobsite, is their strong magnetic properties, as can be seen in the VSM curves shown in Figure 9. It exhibits a magnetic saturation response with a maximum magnetization of 45.61 emu.g^{-1} , and a coercivity of 29 Oe , close to a superparamagnetic behavior, as observed in magnetite nanoparticles (Yamaura et al. 2004).

Although the Jacobsite crystals, at first glance, look like a strongly magnetic material;

the VSM measurements indicated a relatively weak magnetism (Figure 10), reaching a maximum magnetization of 6.96 emu.g^{-1} , keeping the superparamagnetic behavior ($H_c = 9\text{ Oe}$). Despite the unpaired 5 electrons in the Mn(II) ions, the magnetic behavior of Jacobsite is not proportionally strong, implying the occurrence of ferrimagnetic interactions in the crystal. In contrast, the synthetic manganese ferrite nanoparticles exhibited a strong magnetism, consistent with the existence of low interconversion barriers within the nanomagnetic domains, facilitating their orientation in the applied field. Given the complexity of interactions between magnetic domains and their influence on the material's macroscopic properties, further advancement will require advanced characterization techniques, including First Order Reversal Curve (FORC) measurements. As described in the literature (Sasaoka et al. 2023), this technique can offer valuable insights into coercivity distributions and domain interactions that are not accessible through conventional hysteresis measurements. Such investigation, involving different samples and conditions is currently

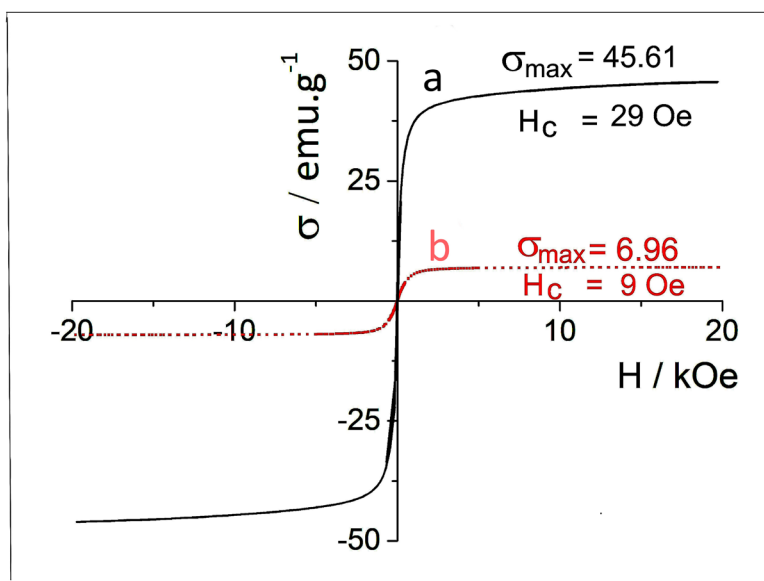


Figure 9. VSM plots for the synthetic manganese-ferrite nanoparticles (a) and Jacobsite (b) show their magnetization saturation behavior of 45.61 and 6.96 emu.g^{-1} , and coercivity $H_c = 29$ and 9 Oe , respectively.

under investigation in our Laboratory and will be the subject of future publications.

The magnetic behavior of the nanoparticles can also be probed by atomic force microscopy, as shown in Figure 10. By using magnetic probes, the manganese-ferrite nanoparticles appear in high contrast, showing typical sizes of about 50-100 nm, in agreement with the light scattering and DRX measurements.

Interaction of the manganese-ferrites with diatoms

Diatoms are single-cell photosynthetic algae exhibiting unusual porous silica shell structures, which are readily available from inexpensive sources, such as diatomaceous earth, allowing many applications in chemistry, physics, biology, and engineering. They have been recently applied in drug delivery in medicine, because their porous structure can host molecules such as indomethacin, for controlled release in the organism. One such interesting application in

drug delivery involves their association with magnetic nanoparticles, which can be guided or maintained in their local application, with the aid of a magnet (Losic et al. 2010).

The diatom shells exhibit negative zeta potentials and can bind positively charged magnetic nanoparticles. For this reason, the manganese-ferrite nanoparticles were treated with 2 M HNO_3 and impregnated with Fe^{3+} ions, as reported in the literature (Tourinho et al. 1990). The modified nanoparticles were found to interact with diatoms, generating interesting biosilicate species which readily respond to the magnet. Some of them have been collected for illustration purposes, using the darkfield images obtained with a CytoViva microscope, as illustrated in Figure 11. Their possible applications are yet under investigation in our laboratory.

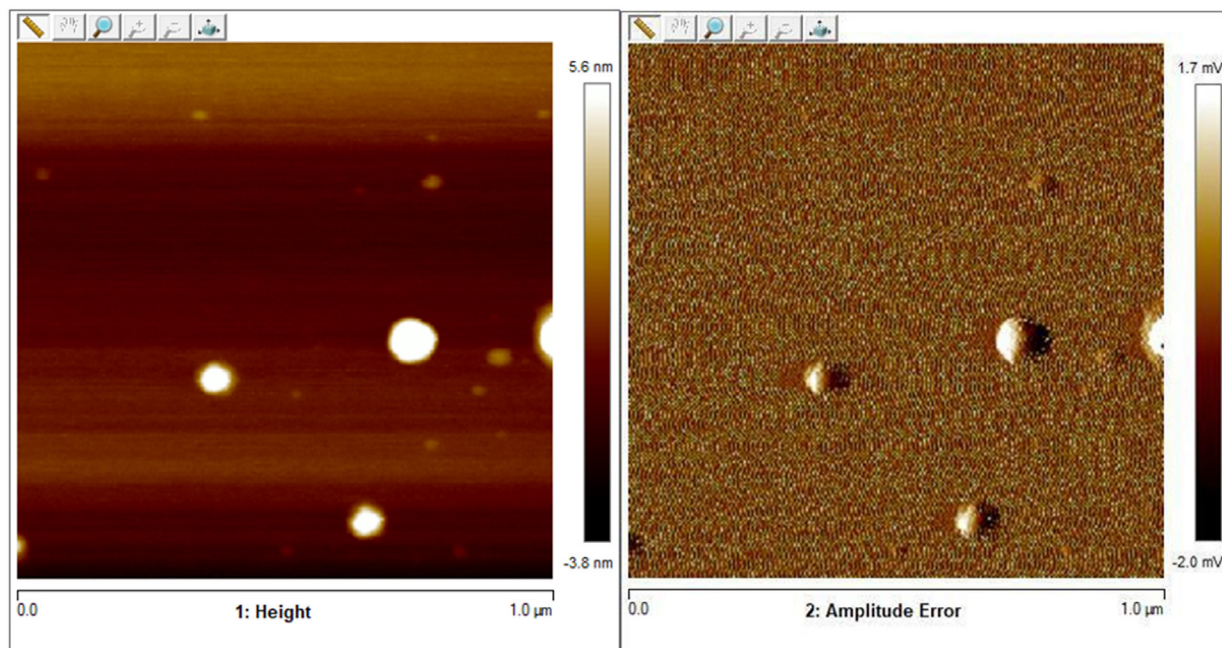


Figure 10. AFM images (left) in the magnetic mode (right) of manganese-ferrite nanoparticles, showing spherical nanoparticles of about 50-100 nm.

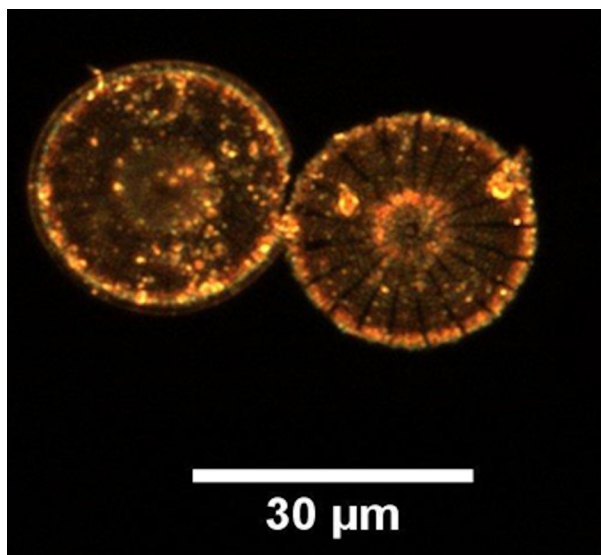


Figure 11. Darkfield image of a diatom shell impregnated with positively charged manganese-ferrite nanoparticles.

CONCLUSION

Manganese-ferrites can be synthesized using the coprecipitation method in the presence of citrate ions, yielding strongly magnetic nanoparticles ($\sigma_{\text{max}} = 45.6 \text{ emu.g}^{-1}$), structurally identical with the magnetite spinell, Fe_3O_4 , and the Jacobsite mineral, MnFe_2O_4 . Their composition indicates the Mn/Fe proportion of 1:2 found in Jacobsite. However, in contrast, the mineral exhibited a rather weak magnetism, indicating a ferrimagnetic coupling in the crystals. Therefore, the synthetic methods provide a better alternative for developing strongly magnetic manganese ferrites. In addition, their nanoparticles can be easily manipulated in aqueous solutions, exhibiting a hydrodynamic radius of about 70 nm, and a Zeta potential of -13 mV. They are reasonably stable up to 400 °C, undergoing a broad exothermic change above this temperature, as monitored by TGA and DTA techniques, yielding new manganese and iron-oxide species. Similar thermal behavior above 400 °C is also observed for Jacobsite. The manganese-ferrite nanoparticles interact

with diatoms, providing interesting magnetic biosilicate carriers for drug delivery.

Acknowledgments

Financial support from Fundação de Amparo à Pesquisa do Estado de São Paulo, FAPESP grant 2018/21489-1, is gratefully acknowledged.

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How to cite

QUARTAROLLI LF, DE MELO FM, MARTINS JM, SILVEIRA-JUNIOR AT, NAKAMURA M & TOMA HE. 2024. New insights on the Jacobsite mineral from Bahia and related synthetic manganese-ferrite nanoparticles. *An Acad Bras Cienc* 96: e20240234. DOI 10.1590/0001-376520240240234.

*Manuscript received on March 13, 2024;
accepted for publication on June 13, 2024*

LUCAS F. QUARTAROLLI

<https://orcid.org/0000-0002-1000-7025>

FERNANDO M. DE MELO

<https://orcid.org/0000-0003-0270-5912>

JOANIEL M. MARTINS

<https://orcid.org/0009-0005-5033-7204>

ALCEU T. SILVEIRA-JUNIOR

<https://orcid.org/0000-0002-1307-6368>

MARCELO NAKAMURA

<https://orcid.org/0000-0002-4434-8469>

HENRIQUE E. TOMA

<https://orcid.org/0000-0002-4044-391X>

Universidade de São Paulo, Instituto de Química,
Av. Prof. Lineu Prestes, 748, Cidade Universitária,
05508-000 São Paulo, SP, Brazil

Correspondence to: **Henrique Eisi Toma**

E-mail: henetoma@iq.usp.br

Author contributions

Lucas F. Quartarolli, Fernando M. Melo, performed the synthesis and characterization of the ferrites, Joaniel M. Martins provided the mineral and supported the discussion, Alceu T. Silveira carried out the DRX, EDX, DLS, Thermal Analysis, and FTIR measurements, Marcelo Nakamura performed the Raman and Cytoviva investigation, Henrique E. Toma was responsible for supervising the research, and writing the manuscript.

