INTRODUCTION

Maghemite (gamma-phase iron oxide, $\gamma$-Fe$_2$O$_3$), especially in a nanoparticle form, has attracted much attention as a soft ferrimagnetic (or superparamagnetic) material with large coercivity (~5-80 mT$^{-1}$) for magnetic recording device, catalysts, magnetic resonance imaging, cancer treatment, and other electronic, biomedical, and environmental applications. While their magnetic properties are well characterized, their nonmagnetic properties are not. Their thermal conductivities have only been measured in the nanofluid form. Their electrical properties have been measured in the composite form, especially with polyaniline (a conductive polymer) for electromagnetic absorbers, and chemical and biological sensor applications. Bulk-scale maghemite samples would be convenient for nonmagnetic property measurement, but the previous work has been mostly focused on nanoparticles.

Cold sintering to form bulk maghemite for characterization beyond magnetic properties

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Abstract

Maghemite nanoparticles have been sought after for electronic, biomedical, and environment applications, for their soft ferrimagnetic properties and large coercivity. While their magnetic properties are well characterized, their nonmagnetic properties are currently not available because maghemite is prepared as nanoparticles and their bulk forms often have contaminants. In this work, thermodynamically unstable maghemite nanoparticles are cold sintered (130-250°C) to form bulk samples with submicron-size grains. Electrical and thermal conductivities of maghemite were evaluated for the first time: $3.5 \times 10^{-7}$ S/m and 0.86-1.30 W/(mK). The relative densities of these cold-sintered samples are low (55.9%-64.2%) but comparable with or slightly lower than those previously achieved with higher sintering temperature (~55% at 500°C and ~76% at 1250°C). Such porous maghemite samples with large surface areas can potentially be used as an anode of lithium-ion batteries, while further densification will be pursued in the future by sintering process modification.

KEYWORDS

characterization, magnetic materials/properties, sinter/sintering

1 | INTRODUCTION

Maghemite (gamma-phase iron oxide, $\gamma$-Fe$_2$O$_3$), especially in a nanoparticle form, has attracted much attention as a soft ferrimagnetic (or superparamagnetic) material with large coercivity (~5-80 mT$^{-1}$) for magnetic recording device, catalysts, magnetic resonance imaging, cancer treatment, and other electronic, biomedical, and environmental applications. These maghemite nanoparticles are synthesized by physical (ball milling and oxidization, deposition, spraying, etc.) and chemical (co-precipitation, sol-gel, etc.) processes. While their magnetic properties are well characterized, their nonmagnetic properties are not. Their thermal conductivities have only been measured in the nanofluid form. Their electrical properties have been measured in the composite form, especially with polyaniline (a conductive polymer) for electromagnetic absorbers, and chemical and biological sensor applications. Bulk-scale maghemite samples would be convenient for nonmagnetic property measurement, but the previous work has been mostly focused on nanoparticles.
Fabrication of densified maghemite has been attempted with powder sintering,12,13 precipitation,14 or sol-gel method,15 but resulted in contaminants, phase transformation (at >500°C), and porosity. Naturally available iron oxide minerals are not purely maghemite and contain other phase and elements.16,17

In this work, ferrimagnetic maghemite nanoparticles are cold sintered to form bulk maghemite samples, without contaminants, consisting of submicron-size grains, so that nonmagnetic property characterization of maghemite can be conducted using macro-scale testing. The spinel face-centered cubic structure of maghemite is thermodynamically unstable and transforms to alpha-phase (α-Fe₂O₃, hematite, antiferromagnetic) when heated to ~250-700°C.18-20 In the cold sintering process, solid particles are mixed with transient solvents, commonly water, and densify based on dissolution, rearrangement/packing, and precipitation of particles under pressure, thus enabling sintering at low temperatures.21-23 Sintering at low temperatures is critical for energy efficiency24 and for sintering of thermodynamically unstable materials.25 So far, solid-state electrolytes and cathodes,26-28 piezoelectric materials,29-31 and other materials for ceramic packing and microwave devices32 were successfully cold sintered. Below, maghemite powders were cold sintered, and the phase transformations of fabricated bulk maghemite samples were characterized, as were the magnetic properties and thermal and electrical conductivities.

2 | EXPERIMENTAL PROCEDURE

2.1 | Cold sintering of maghemite nanoparticles and their densification

Maghemite nanoparticles were purchased (US3200, US Research Nanomaterials, Inc.) and inspected with Fourier transform infrared (FTIR) spectroscopy to confirm that they are maghemite, and not magnetite (Fe₃O₄, also ferrimagnetic) that is, unlike maghemite, thermally stable (565°C Curie temperature33). As shown in Figure 1A, the FTIR spectrum confirmed the peaks at ~620 cm⁻¹ and ~687 cm⁻¹ that are uniquely associated with γ-Fe₂O₃ structure: stretching of partially occupied octahedral iron cation against oxygen.34,35 The maghemite nanoparticle sizes were visually inspected as ~15-25 nm using transmission electron microscopy (TEM, Philips EM 420, see Figure 1B), and their aggregate sizes were quantitatively characterized as ~0.5-10 μm using dynamic light scattering (Zetasizer Nano ZS) and optical microscope (Olympus BX51WI, see Figure 1C). These maghemite nanoparticles were mixed with DI water (20 wt%) using a mortar and pestle, packed into a pellet die (carbon steel, ~12.7 mm diameter disk), and applied with pressure (max. 620 MPa) and temperature (max. 250°C). The cold sintering conditions are summarized in Table 1; temperatures above 100°C were selected to evaporate the water.

2.2 | Electrical and thermal conductivity measurement of cold-sintered maghemite samples

The DC volume electrical conductivity was measured based on ASTM D257. A thin plate (4.5 mm length, 5.3 mm width, and 0.58 mm thickness) was prepared, coated with silver paint, and conditioned at 26°C and 16% humidity for 48 hours. The electrical resistance in the thickness direction was measured from the voltage-current plot (0-500 V with 25 V increment). The thermal conductivity was measured using comparative infrared thermal microscopy.36 A thin plate (6.0 mm length, 2.2 mm width, and 0.5 mm thickness) was cut, sandwiched between two reference gum rubber plate
(3.1 mm thickness, 0.15 W/(mK)), and the heat flux was applied in the thickness direction. The infrared microscopy captured the temperature gradients across the sample stack. The heat flux through the sample system was calculated from the measured temperature gradient and the known thermal conductivity of the reference samples, and the thermal conductivity of the maghemite sample was calculated from the heat flux and the measured temperature gradient.

3 | RESULTS

The relative densities of cold-sintered maghemite samples are listed in Table 1. Their densities were estimated from the measured weight and volume; the relative density was calculated based on the theoretical density of maghemite (4.9 g/cm³). Two samples made using the same condition (130°C and 380 MPa) resulted in similar densities, confirming repeatability of the process. The temperature increase (from 130°C to 250°C) helped densification of the maghemite nanoparticles, while the pressure increase (from 380 MPa to 620 MPa) did not. The fracture surfaces of these samples were inspected using scanning electron microscopy (SEM, FEI NanoSEM 630 FESEM, see Figure 2). When cold sintered at 130°C, the fracture surfaces are rough due to the porosity. When cold sintered at 250°C, the fracture surfaces are less rough; grain growth was observed filling in the gaps between particles.

The effect of cold sintering temperature on the magnetic properties of maghemite was evaluated using X-ray diffraction (XRD, PANalytical Empyrean X-Ray Diffractometer, Co source) and vibrating sample magnetometry (VSM, MicroSense EZ7, ±1200 kA/m). As noted above, the phase transformation from maghemite (spinel face-centered cubic, ferrimagnetic) to hematite (trigonal, antiferromagnetic) is expected when heated at >250°C. Here, the cold-sintered samples (both at 130°C and 250°C) exhibited XRD peaks of maghemite and no new XRD peaks associated with hematite (see Figure 3A). Ferrimagnetic properties of maghemite were maintained after cold sintering as shown in Figure 3B and are compared with the literature values in Table 2. The cold-sintered samples have smaller susceptibility and remanence values than the nanoparticles and the literature values, possibly due to their porosity (air), amorphous grain boundaries formed during cold sintering, measurement resolution limits, or sample shape effects.

The electrical and thermal conductivities of maghemite were estimated from the measurement of the porous cold-sintered sample, its relative density (56.4%), its powder tap porosity (measured as 74%), and the theoretical values of air, as summarized in Table 3. The electrical conductivity of maghemite was estimated using rule of mixture, and the thermal conductivity of maghemite was estimated using both rule of mixtures (lower bound, suitable for very low porosity) and Landauer’s relation (upper bound, suitable for higher porosity). These conductivity measurements can mark as the first available data of maghemite in the literature. In the past, transport properties were measured only about maghemite composites: 10⁻⁷–10⁻² S/m for maghemite-polyaniline nanocomposites with varying

![Figure 2](image-url)
The obtained relative densities of the cold-sintered maghemite samples in this work are low (55.9%–64.2%). While this poor densification can be attributed to the low temperature and thus low diffusion rate, in the past, cold sintering of other oxides has achieved higher relative densities with temperatures lower than 130-250°C: >90% (~100°C, 77-387 MPa) for ZnO, and 77.5-84.5% (30°C, 200-500 MPa) for HBO₂-II. Yet, our work uniquely provides decent densification (55.8-64.2%) with lower temperature (~130-250°C) when compared with previous sintering work of iron oxides: 55% (400-500°C, 200 MPa, maghemite nanoparticles), and ~76% (1250°C, hematite pellets). To improve densification, in the future, multiple steps or reactive transient liquid phases can be introduced to the sintering process, followed by postsintering treatments.

4 | DISCUSSION

The obtained relative densities of the cold-sintered maghemite samples in this work are low (55.9%–64.2%). While this poor densification can be attributed to the low temperature and thus low diffusion rate, in the past, cold sintering of other oxides has achieved higher relative densities with maghemite concentrations and 0.982 W/(mK) for maghemite-water nanofluids with 2.5 vol% of maghemite.

5 | CONCLUSIONS

Cold sintering of thermodynamically unstable gamma-phase maghemite nanoparticles was conducted at low temperature (130-250°C). The cold-sintered maghemite samples were observed with no phase transformation to alpha-phase hematite, and the ferrimagnetic properties were maintained. The resulting relative densities are low (55.9-64.2%) but comparable with or slightly lower than those previously achieved with higher sintering temperature.

| Samples | Relative density (%) | Initial susceptibility (unitless) | Coercivity (mT) | Remanence (mT) | Saturation (emu/g) |
|---------|---------------------|----------------------------------|----------------|---------------|-------------------|
| Nanoparticles | —                  | 4.95                             | 1.41           | 7.1           | 66.1             |
| Cold sintered at 250°C, 380 MPa | 64.2 | 1.30 | 3.07 | 4.3 | 65.1 |
| Cold sintered at 130°C, 380 MPa | 56.4 | 1.42 | 1.88 | 3.1 | 67.6 |
| Reference | —                  | 2.79                             | ~5-80          | ~15-100       | —                |

| Sample | Electrical conductivity [S/m] | Thermal conductivity [W/(mK)] | Relative density [%] |
|--------|-------------------------------|------------------------------|---------------------|
| Cold sintered at 130°C, 380 MPa | $1.03 \times 10^{-7}$ | 0.495 | 56.4 |
| Air | $3 \times 10^{-15}$ | 0.024 | 43.6 |
| Maghemite (estimated) | $3.5 \times 10^{-7}$ | 0.86-1.30 | — |
(~55% at 500°C, and ~76% at 1250°C). The cold-sintered maghemite samples are porous, but bulk and monolithic with submicron-sized grains. Their electrical and thermal conductivities were measured, and those of maghemite were extrapolated for the first time. In the future, the cold sintering processes will be modified to improve densification, by introducing multiple sintering steps, reactive transient liquids, and/or postsintering treatment. Meanwhile, porous maghemite samples with large surface areas can potentially be used in applications such as an anode of lithium-ion batteries.14,15

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