Developing the synthesis and the processing route of metastable magnetic nanocomposites using CAPAD

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Highlights

- We succeed in the synthesis and densification of dense metastable ε- Fe_2O_3 based nanocomposites.
- This sample consists of high coercivity of the dense, large sized magnets and compares favorably with rare earth and precious metal based magnets.

1. Introduction

The new material with attractive properties can be developed via innovative processing approaches. One example is overcoming thermodynamic limits using kinetics to obtain materials with far from equilibrium (FFE) state. Bulk material with nano-sized grains or metastable phase often possesses non-conventional properties. Obtaining FFE bulk materials through powder consolidation approaches, requires the optimizations of (A) the powder synthesis method specifically for the specific consolidation route and (B) the consolidation method to maintain FFE state as bulk form. The necessity of the optimization is because an appropriate energy balance (heat) is required; if FFE materials are overheated, they will convert to equilibrium phase/state and exhibit conventional properties. On the other hand, if the heat is not sufficient, the sample cannot be densified sufficiently therefore it will not have any use as a bulk material. Here we will present results on the chemical synthesis of metastable material/phases and the integration into a consolidated nanocomposite via Current Activated Pressure Assisted Densification (CAPAD). We will show processing of metastable iron oxide/silica bulk magnets. Magnetic properties evidenced the presence of metastable Eplison-Fe_2O_3 in bulk body. The ε-Fe_2O_3 phase is one of the metastable phases of iron oxide and exhibits extremely high coercivity (higher than typical rare-earth-based magnets) but it is difficult to obtain since a synthesis route must have precise control of both temperature and size of the phases. [1-5] Recently Ohkoshi and co-workers introduced a reliable reverse-micelle based powder synthesis route.[6-9] Although there is a strong demand for new magnet bulk material, it is very difficult to produce bulk magnet containing ε-Fe_2O_3 because adding heat to ε- Fe_2O_3 accelerates conversion to a more stable α- Fe_2O_3 phase witch does not exhibit high coercivity.

2. Methods

We used a modified reverse-micelle/sol–gel powder synthesis route [6-9]. Two reverse-micelle solutions were prepared. (A) contains 0.74 mmol of $Fe(NO_3)_3$ and 0.074 mmol of $Ba(NO_3)_2$. (B) contains NH_4OH. Both solution also contains 9.7 mmol cetyltrimethylammonium bromide (CTAB), 39 mmol C_4H_9OH, 110 mmol C_8H_{18}, and 330 mmol H_2O. These solutions were combined to precipitate $Fe(OH_3)$ particles within the reverse-micelles, and tetraethyl orthosilicate (TEOS) was added to form the silica shell (step 1.2 in Fig. 1). Varying amounts of TEOS (a silica forming precursor) was added to attain the desired concentration of Fe–Ba in silica (Si-O), resulting in Fe–Ba concentrations ranging from 15–90 mol%. The ratio of Fe to Ba was maintained at 9 to 1. Since iron oxide (IO) is the major magnetic component, we will henceforth refer to the composites using the terminology IO-XX%, where XX is the mol% of Fe–Ba. Using this scheme, samples IO-15% and IO-90% have 15% (Fe–Ba)/85% Si–O and 90% (Fe–Ba)/10% Si–O content, respectively. The resulting powder was washed with $CHCl_3$ and CH_3OH, centrifuged and dried at 80 °C under vacuum (step 1.3). An additional low-temperature calcination step (step 2, 450–600 °C for 1 h) was used to remove organic residue and to minimize the outgassing during the densification process. The synthesized powder was densified using Current Activated Pressure Assisted Densification (CAPAD). A 9.5 mm inner diameter graphite die and tungsten carbide plunger set was loaded with 0.25 g of the synthesized powder. A pressure of 100–300 MPa was then applied. The system heated up to 450–600℃ at an average

heating rate of 100–300℃ min^{-1} under vacuum. The samples were then kept at the desired load and temperature with hold times ranging between 1–5 minutes before removing the mechanical load and rapidly cooling the sample (step 3). Following the densification, samples were extracted from the graphite die and annealed in air at 1025℃ for one hour (step 4) to attain a bulk IO/silica composites. SEM and XRD were used to characterize microstructure and crystal phase, respectively. Magnetic properties were measured by MPMS-VSM.

3. Results and discussion

We found that applying any sufficient heat to the powder containing ε- Fe_2O_3 phase for densification purpose accelerate the phase conversion to ε- Fe_2O_3. Then the sample showed low coercivity. Therefore we had to modify the powder synthesis route for producing bulk material with the desired property. Most effective optimizations were using powder with Fe-O precoser to densify and selecting rapid densification approach. After densification and annealing, the bulk sample had a relative density as high as 90% and contained 90 mol% of IO, leading to a very high 12 kOe coercivity and the first reported volume magnetization measurements of composites consisting primarily of ε- Fe_2O_3. XRD results supported that main phase was ε- Fe_2O_3. SEM revealed that the bulk sample post densification process (step 3) maintained very fine nano size granule grains which grown to form rod shape after annealing(step 4). Table 1 shows the composition of IO, the density of bulk sample pre/post-annealing and its coercivity. The dimension of bulk material was about ϕ 9.5mm * 2mm. The high coercivity of the dense, large sized magnets compares favorably with rare earth and precious metal based magnets. It is possible that high ε- Fe_2O_3 content composites could be used in conjunction with aligning and exchange coupling as has been shown in high-performance rare earth-based magnets. Thus results presented here should be useful for the development and implementation of a wide range of bulk nanocomposites based on earth-abundant, environmentally friendly components

Table 1 The composition of IO, the density of bulk sample pre/post annealing and its coercivity

Mol% IO (Fe–Ba)	Density-pre anneal (%)	Density-post anneal (%)	Coercivity (kOe)
15	94.1	93.9	15.0
40	88.4	88.7	15.0
75	83.9	84.2	12.5
90	89.0	87.1	12.0

4. Conclusions

We presented a synthesis and processing procedure for the production of dense metastable ε- Fe_2O_3 based nanocomposites. XRD and Magnetic properties evidenced the presence of metastable ε- Fe_2O_3 in bulk body. SEM showed that the sample consisted of nano size composite structure.

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Keywords
"CAPAD" "Metastable material" "nano composite"