Novel microwave assisted chemical synthesis of Nd$_2$Fe$_{14}$B hard magnetic nanoparticles

Viswanathan Swaminathan, Pratap Kumar Deheri, Shekhar Dnyaneswar Bhide and Raju Vijayaraghavan Ramanujan*

The high coercivity and excellent energy product of Nd$_2$Fe$_{14}$B hard magnets have led to a large number of high value added industrial applications. Chemical synthesis of Nd$_2$Fe$_{14}$B nanoparticles is a challenging due to the large reduction potential of Nd$^{3+}$ and the high tendency for Nd$_2$Fe$_{14}$B oxidation. We report the novel synthesis of Nd$_2$Fe$_{14}$B nanoparticles by a microwave assisted combustion process. The process consisted of Nd–Fe–B mixed oxide preparation by microwave assisted combustion, followed by the reduction of the mixed oxide by CaH$_2$. This combustion process is fast, energy efficient and offers facile elemental substitution. The coercivity of the resulting powders was ~8.0 kOe and the saturation magnetization was ~40 emu g$^{-1}$. After removal of CaO by washing, saturation magnetization increased and an energy product of 3.57 MGOe was obtained. A range of magnetic properties was obtained by varying the microwave power, reduction temperature and Nd to Fe ratio. A transition from soft to hard magnetic properties was obtained by varying the composition of Nd$_2$Fe$_{14}$Ba (x varies from 7% to 40%). This synthesis procedure offers an inexpensive and facile platform to produce exchange coupled hard magnets.

1 Introduction

Rare earth (RE)-transition metal based high energy density magnets are of immense significance in various engineering applications.$^1$ Nd$_2$Fe$_{14}$B magnets possess the highest energy product and are widely used in electric motors, generators, magnetic separators, magnetic levitation systems, micro motors, MEMS and memory applications.$^2,3$ Physical methods such as ball milling and melt spinning are well studied and utilized in industrial scale production. However, these methods have several limitations including high energy consumption, the requirement of high purity metals and inhomogenous microstructure. Hence, there is a need to explore new methods for synthesis of magnetic nanomaterials.

Novel chemical synthesis methods for Nd$_3$Fe$_{14}$B based magnets have attracted considerable attention, since magnetic properties such as energy product and coercivity can be tuned by controlling the microstructure, crystal orientation and annealing conditions.$^4,5$ Dong et al.$^6$ have reported mechano-chemical synthesis of 1 μm size Nd–Fe–B particles sequentially using pyrolytic decomposition, debinding, milling and reduction–diffusion (R–D) and washing of CaO. Although Nd–Fe–B alloys with a particle size of 30–100 nm were produced by Haik et al.$^7$ using boro-hydride reduction, the resulting powders exhibited soft magnetic properties; a coercivity of 200 Oe and a saturation magnetization ($M_s$) of 24 emu g$^{-1}$ were reported. In another study,$^8$ thermal decomposition and boro-hydride reduction were used to produce α-Fe powders and Nd$_2$Fe$_{14}$B powders, respectively. Exchange coupled Nd$_2$Fe$_{14}$B/α-Fe nanocomposites were then prepared from these powders by self-assembly using a surfactant. Nd$_2$Fe$_{14}$B alloys have also been prepared by the reduction of Nd$_2$O$_3$, Fe and B powders with CaH$_2$, followed by sintering. Uncontrolled particle growth resulted in the formation of micron size Nd$_2$Fe$_{14}$B powders.$^9$ This size is not optimum for hard magnetic properties; extrinsic magnetic properties such as coercivity and remanent magnetization are controlled by the particle size and shape; coercivity reaches a maximum at a particle size corresponding to single domain formation.$^9$

Moreover, the reduction potential of Nd$^{3+}$ is high and Nd–Fe–B alloys tend to oxidize very easily even in the bulk form.$^{10,11}$ Hence, the synthesis of nanoparticles of these alloys is challenging. Nanoparticle synthesis can also be used to enhance exchange coupling and to obtain high energy product nanocomposite magnets. Nd$_2$Fe$_{14}$B and α-Fe nanocomposites are attractive because the high coercivity of the hard magnetic phase and high saturation magnetization of the soft magnetic phase leads to high energy product permanent magnets.$^{12–15}$ Lower cost Nd-oxide or NdCl$_3$ salts rather than pure Nd metal can be used in chemical synthesis based on R–D methods. “Bottom-up” molecular level assembly of atoms by chemical synthesis results in uniform composition and the crystal structure appropriate for
hard magnetic properties. Chemical methods such as electrodeposition, the hydrogenation–disproportionation–desorption–recombination (HDDR) process, the mecanochemical process, boro-hydride reduction, the solid state reaction method and the sol–gel method have been used to produce Nd–Fe–B alloys. However, these methods have had limited success in the production of Nd–Fe–B nanostructures.

Microwave assisted syntheses of other nanoparticles have been reported earlier. Using microwave synthesis to obtain the desired properties is of high research interest. We report the facile synthesis of Nd2Fe14B nanoparticles by the microwave assisted combustion technique. Microwave synthesis possesses several advantages including molecular level mixing, faster reaction compared to solid state processes, energy efficiency and the potential for large scale production. The process involves Nd–Fe–B oxide preparation by the microwave technique, followed by the reduction of the Nd–Fe–B oxide by Ca or CaH2. As compared to the sol–gel synthesis method, no extra heating steps are required to obtain the Nd–Fe–B oxide powder in this microwave synthesis method.

This process can also be extended to produce other permanent magnet materials such as SmCo5, FePt, Dy–Fe–B or Nd2Dy1–xCaxB/FeCo systems. To the best of our knowledge, this work is the first report on the synthesis of Nd2Fe14B nanoparticles using the microwave process.

### 2 Results and discussion

#### 2.1 Reduction diffusion process

The microwave assisted combustion synthesis method is similar to the auto-combustion method. Here, the initiation of combustion is achieved by a microwave oven. Microwave irradiation of the solution caused evaporation of water. Metal nitrates reacted spontaneously with glycine producing Nd–Fe–B oxide powders. The reaction scheme of Nd–Fe–B oxide formation by glycine–nitrate combustion (salt to glycine molar ratio of 1 : 1) is shown in the following reaction (Reaction (1)). The Nd–Fe–B oxide was found to be a mixture of NdFeO3, Fe3O4, FeO, B2O3 and NdBO3 (Table 1).

#### Table 1 Reduction mechanism and magnetic properties of Nd–Fe–B synthesized by microwave assisted combustion synthesis

<table>
<thead>
<tr>
<th>Reduction temperature (°C)</th>
<th>Material identified from Rietveld refinement</th>
<th>Composition (weight %)</th>
<th>Magnetic measurement (° before washing, • after washing)</th>
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<tr>
<td></td>
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<td>Coercivity (Oe)</td>
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<tr>
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<td>Nd2FeO3</td>
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<td>800 Nd–Fe–B oxide + 0.2 wt% B</td>
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The Nd–Fe–B oxide powders were then reduced by CaH₂ in the temperature range of 400 °C to 800 °C. The phases present were analysed by XRD and the mass percentage was calculated from Rietveld refinement (Table 1). The reduction of iron oxides (Fe₃O₄ and FeO) to form α-Fe was initiated at 400 °C; a larger mass fraction of iron oxide was reduced at 500 °C. At 600 °C, the ternary NdFe₄B₄ and Nd₂Fe₁₇ phases were identified, suggesting that the Nd₂Fe₁₄B formation mechanism may be different from the mechanism observed in sol–gel synthesis.³¹,³²

The coercivity of the starting precursor is low (225 Oe). The increase in coercivity of the Nd–Fe–B powder reduced at 400 °C is due to α-Fe phase formation (Table 1). The slight decrease in coercivity of the powder reduced at 500 °C is due to α-Fe grain growth. The formation of Nd₂Fe₁₇ at 600 °C resulted in a slight increase in coercivity. At a reduction temperature of 700 °C, the rate of diffusion increased and the desired Nd₂Fe₁₄B phase formed. A high mass percent of the desired Nd₂Fe₁₄B phase along with Nd₂Fe₁₇, α-Fe and by-product CaO phases were formed at a reduction temperature of 800 °C (Fig. 1A). The increase in coercivity for reduction temperatures 700 °C and 800 °C is due to the formation of the high coercivity Nd₂Fe₁₄B phase. The nonmagnetic CaO was removed by washing with water and dilute acetic acid. The reduction reaction of Nd–Fe–B oxides at 800 °C is Reaction (2):

\[
2\text{Nd(NO}_3)_3 + 5\text{Fe(NO}_3)_3 + 3\text{B(NO}_3)_3 +20\text{C}_2\text{H}_5\text{NO}_2 + 7\text{O}_2 \rightarrow \text{NdFeO}_3 + \text{Fe}_3\text{O}_4 + \text{FeO} + \text{B}_2\text{O}_3 + \text{NdBO}_3 + 25\text{N}_2 + 40\text{CO}_2 + 50\text{H}_2\text{O} \quad (1)
\]

\[
7\text{NdFeO}_3 + 8\text{Fe}_3\text{O}_4 + 29\text{FeO} + \text{NdBO}_3 + \text{B}_2\text{O}_3 + 88\text{CaH}_2 \quad \text{800 °C} \rightarrow 3\text{Nd}_2\text{Fe}_{14}\text{B} + \text{Nd}_2\text{Fe}_{17} + \text{Fe} + 88\text{CaO} + 176\text{H}_2 \quad (2)
\]

However, the Nd₂Fe₁₇ mass percent is ~10.6 wt% due to boron loss during reduction as volatile boron hydride. The Nd₂Fe₁₇ mass percent could be reduced to 5 wt% by 0.2 wt% of amorphous boron addition to the Nd–Fe–B oxide and CaH₂ mixture (Table 1). The magnetic properties improved as the mass percent of Nd₂Fe₁₄B increased, the coercivity increased from 5.9 kOe to 8 kOe and the saturation magnetization increased from 31 emu g⁻¹ to 40 emu g⁻¹ (Fig. 2A, Table 1).

The saturation magnetization increased but the coercivity decreased after CaO removal by washing with water (Fig. 2B, Table 1), as observed previously for the sol–gel synthesis method.³³ However, no Nd₂Fe₁₄Bₓ phases were observed by XRD. The mass percentage of the Nd₂Fe₁₄Bₓ phase and the value of x are dependent on the wt% of CaH₂ used for reduction.³³ Rietveld refinement of CaO removed Nd–Fe–B powder, spiked with 10 wt% of standard CeO₂ showed that the Nd–Fe–B powder consisted of ~13 wt% of the amorphous phase (Fig. 3). Hydrogenation caused amorphization of the Nd₂Fe₁₄B phase.³⁴,³⁵

High resolution TEM substantiated this observation by revealing an amorphous phase at the grain boundaries (Fig. 4). This amorphous phase resulted in changes in the intergranular...
magnetic interactions, decreasing remanent magnetization and energy product.\textsuperscript{35} The average crystallite size calculated from Rietveld refinement was \( \sim 80 \) nm. Nd\(_2\)Fe\(_{14}\)B lattice parameters calculated from Rietveld refinement were found to be \( 'a' = 0.8805 \) nm and \( 'c' = 1.2195 \) nm; the \('a'\) value was comparable with earlier reports; a decrement of 0.01 Å was observed for the \('c'\) value.\textsuperscript{36} The interatomic distance between Fe to Fe nearest neighbours can be correlated with the magnetic moment of Nd\(_2\)Fe\(_{14}\)B; a Nd\(_2\)Fe\(_{14}\)B unit cell resembling a sandwich structure was constructed by Diamond software using Rietveld analysis (Figure 5a and b).

There are six types of Fe sites in the Nd\(_2\)Fe\(_{14}\)B tetragonal phase. The shortest interatomic distances of Fe sites are Fe (k2)–Fe (J1) (2.39 Å) and Fe (J1)–Fe (J1) (2.44 Å).\textsuperscript{37} However, in this present study the shortest atomic distances were found to be 2.3806 Å and 2.4250 Å and were slightly less than the reported values. This decrease in interatomic distance results in the intrinsic magnetic moment reduction.\textsuperscript{37,38}

2.2 Effect of microwave power

Microwave irradiation leads to rapid heating. Varying the microwave power changes the heating rate,\textsuperscript{39} resulting in a change in nucleation and growth rates of Nd–Fe–B particles. In turn, this can alter the size and shape of the particles. The magnetic properties depend on the particle size and shape and thus the magnetic properties can be controlled by microwave power. The mechanism of heat generation in the microwave by dielectric heating is due to the microwave absorption by water molecules. When the intensity of the microwave power increased from 80 to 800 watts, heat generation increases rapidly (eqn (3)). Hence there is a change in the thermal energy, resulting in a change in nucleation and growth rates of Nd–Fe–B oxide particles, which in turn leads to Nd–Fe–B particles of different sizes and shapes (Fig. 6). This size and shape variation alters the magnetic properties of the NdFeB alloys.

\[
P = \sigma |E|^2 = \omega \varepsilon'' |E|^2
\]

Where \( P \) is the microwave power dissipation, \( E \) is the electric field, \( \sigma \) is the total current, \( \omega \) is the frequency of the applied field, \( \varepsilon_0 \) and \( \varepsilon'' \) are the dielectric constants of free space and the imaginary part of the dielectric constant, respectively.

In this work, controlling the NdFeB nanocomposite growth is associated with the heat produced by the input of microwave power; this heat drives the chemical reaction. Growth of nanoparticles can be controlled by changing the microwave power which varies the rate of temperature change and the maximum...
temperature achieved. In turn, these factors control the nucleation and growth of the particles, which determines the size and shape of the particles. Hence, microwave power produced different shapes and sizes of nanoparticles. Since magnetic properties are a function of shape and size, this results in a change in the NdFeB final energy product.

At a lower power of 80 W, the produced powder possessed an equiaxed morphology with an average size of ~20 nm (Fig. 6A). As the power increases to 400 W, long nanorods were observed (Fig. 6B). The selected area diffraction pattern (SADP) of the nanorods can be indexed to Nd$_2$Fe$_{14}$B (Fig. 6B-inset). At a higher power of 800 W, an inhomogeneous morphology consisting of clusters of nanorods and equiaxed morphology was observed (Fig. 6C). For the first time, the relationship between microwave power and magnetic properties of Nd–Fe–B was examined (Fig. 7). A highest $H_c$ of 8.0 KOe and $M_s$ of 40 emu g$^{-1}$ were
obtained for materials reduced at 800 °C with an intermediate microwave irradiation power of 400 watts. The highest energy product \((BH_{\text{max}})\) was obtained for 400 W microwave power due to the formation of exchange coupled hard magnetic nanorods. At low microwave power \(\text{Nd}_2\text{Fe}_{14}\text{B}\) is equiaxed. At 400 W power \(\text{Nd}_2\text{Fe}_{14}\text{B}\) has the shape of nanorods; the coercivity is high due to shape anisotropy, resulting in high \((BH_{\text{max}})\). However, 800 W microwave power resulted in inhomogeneous morphology and low \((BH_{\text{max}})\).

2.3 Compositional effect

Fig. 8A and B illustrates the variation of coercivity and magnetic moment of \(\text{Nd}_x\text{Fe}_{92-x}\text{B}_8\) powders (where \(7 < x < 40\)). The properties could be tuned from soft to exchange coupled (hard/soft) to hard magnetic with increasing ‘x’. The coercivity of the NdFeB powder increased as the concentration of Nd increases. The maximum coercivity was obtained for \(\text{Nd}_{35}\text{Fe}_{57}\text{B}_8\), beyond which the coercivity decreased to 6.1 kOe for a higher concentration of Nd (Nd, 40 at%). This is due to the higher mass fraction of non-magnetic phases of Nd and Nd\(_x\)O\(_3\) at the grain boundaries and smaller mass fraction of the magnetic phase of \(\text{Nd}_2\text{Fe}_{14}\text{B}\). Highest \(H_c\) (higher Nd concentration) and \(M_r\) (less Nd content) were obtained for as-reduced \(\text{Nd}_{35}\text{Fe}_{57}\text{B}_8\) and \(\text{Nd}_2\text{Fe}_{88}\text{B}_8\) powders. The highest energy density \((BH_{\text{max}})\) was obtained for \(\text{Nd}_{13}\text{Fe}_{27}\text{B}_8\), but this composition does not show the highest coercivity and magnetization. This is because the desired mass fractions of hard and soft phases were exchange coupled resulting in \(M_r/M_s\) equal to 0.56, \(M_r/M_s\) is called reduced remanence and is \(\leq 0.5\) for isotropic magnets. Reduced remanence greater than 0.5 indicates that the magnetic phases are exchange coupled.\(^{41-44}\) A smaller mass fraction of non-magnetic phases and the appropriate size of hard and soft magnetic phases increased the energy product for this composition.

3 Experimental procedures

The starting materials were iron nitrate nonahydrate (Alfa Aesar, 98–101%), neodymium nitrate hexahydrate (Alfa Aesar, 99.9%), boron (Alfa Aesar, 99.8%), glycine (Sigma Aldrich, >99%) and calcium hydride (Alfa Aesar, 92%). For example, for a target composition of \(\text{Nd}_{27.5}\text{Fe}_{77.5}\text{B}_7\), the calculated amounts of iron nitrate nonahydrate, neodymium nitrate hexahydrate and
boron (dissolved in 4 N HNO₃ solution) were dissolved in deionized water. Glycine was added to the salt solution in a molar ratio of 1 : 1 (salt : glycine) to obtain a stable sol. The solution was then subjected to microwave irradiation at a low microwave power of 400 W for 10 min and a dark-red viscous product was obtained using a Sharp, R-899R household microwave oven. Microwave heating of the viscous precursor resulted in evaporation of water and other volatiles. Due to the exothermic reaction of nitrate salts and glycine the precursor was spontaneously converted to ultra fine Nd–Fe–B oxide powders.

The desired NdₓFe₁₄₋ₓB nanoparticles were then synthesized by mixing the Nd–Fe–B oxide powder with CaH₂ (Nd–Fe–B oxide : CaH₂ in the mass ratio of 1 : 1.1) and annealing in a vacuum. Reduction was then carried out in the temperature range of 400 °C to 800 °C for 2 h. The resulting powders were washed with deionized water and dilute acetic acid to remove the non-magnetic CaO by-product and later by acetone to remove water; this was followed by vacuum drying to obtain the dried powder.

The washed powders were characterized by X-ray powder diffraction using a Bruker diffractometer (D8-Advance) with CuKα radiation of wavelength 1.5414 Å. Diffraction patterns were recorded with a step size of 0.01°, scan speed of 1 s per step and scan angle 2θ from 20° to 120°. Rietveld refinement was carried out using TOPAS.4.13 A Pseudo-Voigt function was used to model the peak profile; crystallographic parameters such as background, zero point shift, scale factor, unit cell constant, and crystal size were refined. The microstructure of washed samples was studied using a JEOL 2010 Transmission Electron Microscope (TEM). The magnetic properties were measured by a Lakeshore-7404 Vibrating Sample Magnetometer (VSM) which was operated at a maximum magnetic field strength of 1.5 T due to limitations of our equipment. In addition to the reduction diffusion process, Nd–Fe–B synthesis by a microwave assisted hydrothermal route was studied by varying the microwave power in the range of 100 W to 800 W, the effect of composition on the final product was studied by varying the weight percentage of Nd to Fe in the range of NdₓFe₀₂₋ₓB₈ (where 7 < x < 49).

Conclusions

In summary, NdₓFe₁₄₋ₓB nanoparticles were successfully synthesized by a novel, fast and energy efficient microwave synthesis based technique.

- The powders reduced at 800 °C resulted in the desired tetragonal NdₓFe₁₄₋ₓB phase (a = 0.8805 nm and c = 1.2195 nm).
- The Nd–Fe–B powder consisted of the desired NdₓFe₁₄₋ₓB (85.1 wt%), x–Fe (1.9 wt%) phases as well as the amorphous NdₓFe₁₄₋ₓBH₄ (13 wt%) phase.
- Addition of 0.2 wt% of B resulted in a decrease in the mass percentage of the NdₓFe₁₄₋ₓB phase and improved the hard magnetic properties.
- NdₓFe₁₄₋ₓB₈ nanoparticles exhibited an energy product of 3.57 MGOe, which is considerably lower than that of bulk permanent magnets of the same material.
- Formation of amorphous NdₓFe₁₄₋ₓBH₄ at grain boundaries resulted in low remanent magnetization and energy product.
- Tuning of the Nd–Fe–B particle size and magnetic properties could be readily obtained by microwave power.
- The effect of alloy composition showed that a transition from soft to exchange coupled to hard magnetic properties could be obtained by varying the ratio of Nd to Fe from 1.3 to 12.

Acknowledgements

RVR dedicates this work to the memory of his mother, Mrs. Susila Vijayaraghavan.

References

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