



One Pot Synthesis of Exchange Coupled $\text{Nd}_2\text{Fe}_{14}\text{B}/\alpha\text{-Fe}$ by Pechini Type Sol–Gel Method

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In this work, a combination of nanoparticles of $\text{Nd}_2\text{Fe}_{14}\text{B}$ hard magnetic phase and $\alpha\text{-Fe}$ soft magnetic phase were synthesized by one pot chemical synthesis technique using sol–gel method. A gel of Nd-Fe-B was prepared using $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, H_3BO_3 , citric acid, and ethylene glycol by pechini type sol–gel method. The gel was subsequently calcined and annealed to obtain the mixed oxide powders. The produced metal oxide particles were identified with XRD, SEM, TEM to obtain the crystal structure, shape and domain structure of them. The nanoparticles of mixed phase of $\text{Nd}_2\text{Fe}_{14}\text{B}/\alpha\text{-Fe}$ were obtained from these oxides by a process of reduction-diffusion in vacuum by employing CaH_2 as reducing agent. During this process it was optimized by controlling temperature, reaction time and concentration of the reducing agent (CaH_2). The phase formation of $\text{Nd}_2\text{Fe}_{14}\text{B}$ was resulted by the direct diffusion of NdH_2 , Fe and B. The magnetic property of produced hard and soft phases was successfully identified with vibrating sample magnetometer (VSM). The mixed domains of the hard and soft phases were identified with selected area electron diffraction method (SAED) patterns.

Keywords: Hard Magnet, Soft Magnet, Exchange Spring Magnet, Ferromagnetic Exchange Coupling, Pechini Type Sol–Gel, Reduction-Diffusion.

1. INTRODUCTION

Research in the area of magnetism and magnetic materials is solely a combination of fabrication, characterization, theoretical concepts and engineering applications.¹ Since the discovery of the excellent magnetic properties of $\text{Nd}_2\text{Fe}_{14}\text{B}$, intense research has been focused on magnetic properties of nanostructured Fe-rich rare-earth magnetic alloy, its novel synthesis techniques and optimum micro structural development.² Powder metallurgy and rapid quenching are the most commonly used techniques to synthesize $\text{Nd}_2\text{Fe}_{14}\text{B}$ which require high purity starting materials and intensive energy.³ Magnetic particles of $\text{Nd}_2\text{Fe}_{14}\text{B}$ with desired shape and size distribution are used to explore anisotropy, magnetism of single domain particles and exchange coupling.^{4,5} A great interest for researchers lies in magnetic nanoparticles because of their wide range of disciplines like magnetic fluids, energy conversions, magnetic

resonance imaging, catalysis, environmental remediation, data storage, biotechnology and biomedicine.^{6,7} The characteristic magnetic behavior of magnetic nanoparticles is a result of both, the interactions among them and the intrinsic properties of the particles.⁸ Some of the parameters that critically influence the magnetic properties of the nanoparticles are the distribution of the sizes, surface defects, shapes and phase purity; hence the investigation of the magnetism in small particles becomes a complicated task.⁴ Synthesis of the monodispersed nanoparticles with a controlled composition, well-defined shape, tunable interparticle separations, ideal chemical stability and a functionalizable surface still remains a great challenge in the field of nanomagnetism.⁵ A success in such controlled preparation of the particles will tremendously facilitate the great discrimination among finite-size effects, surface effects and interparticle interactions.⁵ Enhanced remanence and increased maximum energy product can be achieved in nanocomposite exchange coupled soft/hard magnet systems by the combination of high magnetization in the soft magnet and high coercivity in the hard magnet.^{9,10}

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This coupling effect between the hard and the soft magnetic materials makes it possible to create materials with improved energy product $(BH)_{\max}$ not achievable in single phase materials.¹¹ Exchange coupling supplies the extra anisotropy which is needed for magnetization stabilization and thus generates magnetically stable nanoparticles.⁵ Exchange biased magnets have been used in the applications such as spintronics and recording media.⁵

Nd₂Fe₁₄B alloy is reactive and prone to oxidation hence its synthesis with controlled size and magnetic moment is quietly challenging.^{12–14} The oxidation problem in metallic particles in nano regime is due to their intrinsic instability over longer periods of time.¹⁵ These nanoparticles also tend to form agglomerates reducing the energy associated with their high surface area to volume ratio.¹⁶ The oxidation of naked metallic nanoparticles in air causes the loss of magnetism and dispersibility.¹⁶ It is much important to develop the protection strategies for chemical stability of magnetic nanoparticles against magnetic degradation during and after the synthesis.¹⁷ The chemical synthesis routes have recently been employed to synthesize nanostructured permanent magnetic materials.^{8, 18–23} The chemical synthesis of Nd₂Fe₁₄B has also been attempted by the reduction of suitable salts of iron and neodymium with sodium borohydride.^{18, 19} Another chemical way is the polyol reduction in which a polyalcohol serves as a reducing agent to reduce the organometallic complex of iron and neodymium.^{20, 24} In chemical synthesis the nanoparticle size can be controlled by adjusting the reaction parameters such as time, concentration of reagents and temperature.²⁵ The chemical synthesis of Nd₂Fe₁₄B by a solution phase method followed by high temperature reduction-diffusion method has been reported previously.^{18–22} In this work we used the metal precursors for Nd:Fe:B in stoichiometric composition 2:14:1 and used the sol–gel method to synthesize the chemically homogeneous oxides of metals (Nd, Fe and B). The reduction-diffusion of these oxides at elevated temperatures resulted in Nd₂Fe₁₄B and α -Fe powders. Here the preparation of Nd₂Fe₁₄B was done by the modified process reported by Deheri et al.²¹ The ratio of metal precursors was modified to get the appropriate amount of α -Fe soft phase necessarily needed for the purpose of exchange coupling. The reaction conditions such as temperature and pH were modified to obtain the fine and non agglomerated nanoparticles. The ratio of CaH₄ to metal ions was modified during reduction to increase their surface area in contact.

2. EXPERIMENTAL PROCEDURES

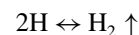
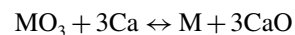
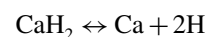
2.1. Synthesis of Nd–Fe–B Oxides by Sol–Gel Method

Neodymium chloride hexahydrate (NdCl₃ · 6H₂O, 99.9%, Sigma Aldrich), iron chloride hexahydrate (FeCl₃ · 6H₂O, Acros), boric acid (H₃BO₃, 99.5%, Duksan), citric acid monohydrate (C₆H₈O₇, 99.5%, Sigma Aldrich) and

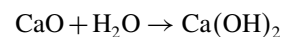
ethylene glycol (C₂H₆O₂, 99.8%, Sigma Aldrich) were used to synthesize Nd–Fe–B gel without further purification. Pechini-type sol–gel method was adopted in preparation of the metal (Nd, Fe, and B) oxides. In this process, the common metal salts are used as precursors and citric acid is used as chelating ligands of metal ions. Polyhydroxy alcohol is used as a cross-linking agent to form a polymeric resin on molecular level. This reduces the segregation of particular metal ions and ensures the compositional homogeneity. This process overcomes most of the difficulties and disadvantages that frequently occur in the alkoxides based sol–gel process. In this experiment, stoichiometric amounts of neodymium chloride hexahydrate, iron chloride hexahydrate and boric acid for the nominal composition of Nd₂Fe₁₄B were dissolved in deionized water to form an aqueous solution. Another aqueous solution of citric acid and ethylene glycol in a 2:1 molar ratio to metal salts was prepared separately and added to the solution of metal salts to form a thermally stable sol. The pH value of the solution remained in the range of 1.9~2. The mixed solution was heated at 90 °C for evaporation purposes which resulted in a viscous gel. The gel was dehydrated at 200 °C for 2 hrs. This dried gel was ground in an agate mortar for 20 min and then heated at 400 °C for 2 hrs for calcination followed by annealing at 800 °C for 2 hrs to prepare Nd–Fe–B oxide powder. The oxide powder was then characterized by X-ray diffraction. This powder was further subjected to reduction-diffusion process to obtain the desired Nd₂Fe₁₄B phase.

2.2. Nd₂Fe₁₄B Synthesis

Nd₂Fe₁₄B powder was synthesized by mixing Nd–Fe–B oxide powder with 1:1 wt% of reducing agent CaH₂ (95%, Sigma Aldrich) and annealing at 800 °C for 2 hrs in vacuum at increasing rate of 6 °C/min. During the process of reduction the chemical reactions took place as;²¹



The pulverization caused by the release of hydrogen gas during heating, resulted in the higher surface area of oxide particles in contact with the reducing particles, which accelerated the process of reduction. The calcium oxide with residual calcium metal was a major by-product in the reaction. For the removal of CaO, the reaction mixture was washed with dilute acetic acid and deionized water. Chemical leaching out of CaO may be shown as;²¹



Finally, the powder was washed with acetone and stored in *n*-hexane. A schematic diagram of the synthesis process is shown in Figure 1.

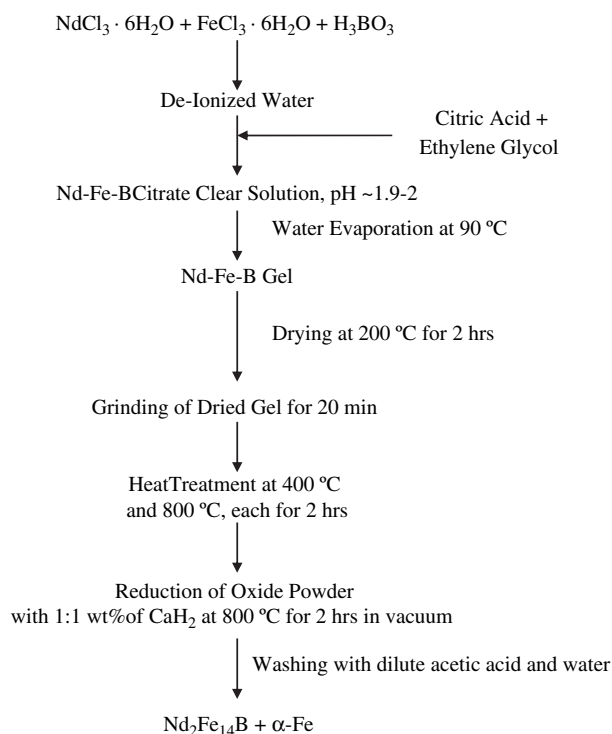
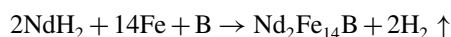
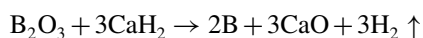
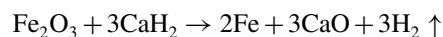


Fig. 1. The flow chart of formation of Nd₂Fe₁₄B/ α -Fe via sol-gel method followed by high temperature reduction-diffusion process.

The mechanisms of chemical reactions involved in the reduction process may be expressed as:²¹



2.3. Characterizations

The X-ray diffraction patterns of the powdered samples were obtained by using Cu-K α radiation ($\lambda = 1.54056 \text{ \AA}$) in a Rigaku X-ray diffractometer at a scanning rate of 0.02° per second in the 2θ range of $20^\circ \leq 2\theta \leq 80^\circ$. The X-ray diffractometer was operated at 40 kV and 150 mA.

The size and shape of the synthesized nanoparticles were analyzed with JEOL, JEM-2010 transmission electron microscope (TEM) operating at 200 kV. For TEM observations, a small amount of the powder sample was dispersed into ethanol and a drop was placed over a carbon coated microscopic copper grid (300 mesh size). The TEM grid was then dried under an IR lamp. The TEM micrograph, EDS, HRTEM and SAED patterns were recorded.

The hysteresis loop was obtained by using Quantum Design 6000 Physical Property Measurement System (PPMS).

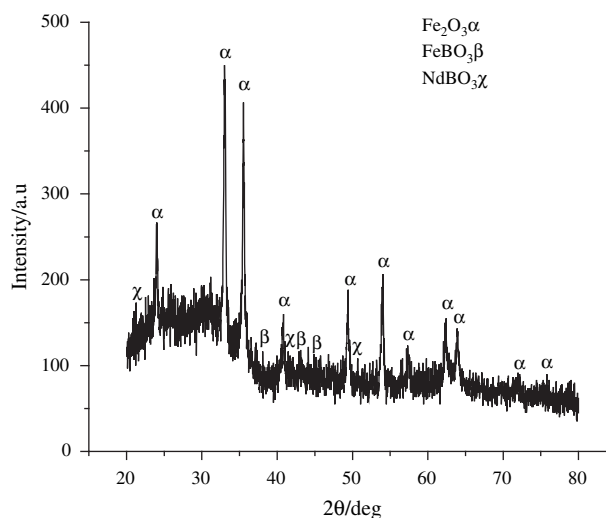


Fig. 2. The XRD pattern of NdFeB gel calcined at 400°C for 2 hrs. In the pattern the three phases of Fe_2O_3 , FeBO_3 and NdBO_3 were identified.

3. RESULTS AND DISCUSSION

The synthesis of Nd₂Fe₁₄B phase was completed in two step processes. In first step, the Nd-Fe-B-oxides were prepared by a modified Pechini type sol-gel method. In second step, the reduction-diffusion of the metal oxides was carried out by using CaH₂ as reducing agent. The method was advantageous controlling the kinetics of the reaction to yield ultra fine metallic powder, preferring the particle nucleation over particle growth. The reaction conditions such as solution concentration, CaH₂/metal ion ratio and pH, decisively influenced the reaction procedure and affected the properties of the final product including composition, morphology, particle size and particle size distribution.

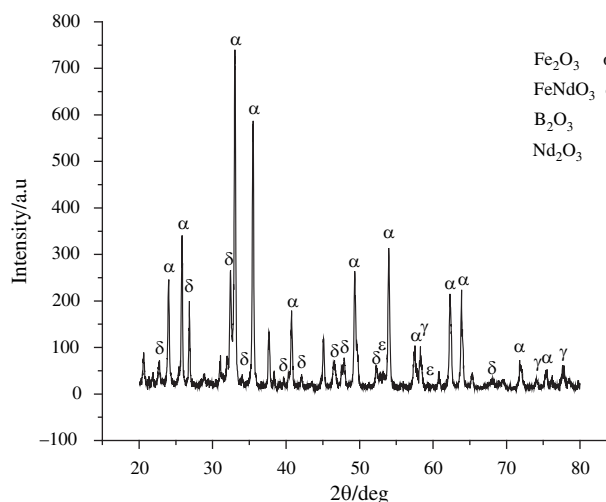


Fig. 3. The XRD pattern of NdFeB oxide powder annealed at 800°C for 2 hrs. In the pattern the four phases of metal oxides Nd_2O_3 , B_2O_3 , Fe_2O_3 and NdFeO_3 were identified.

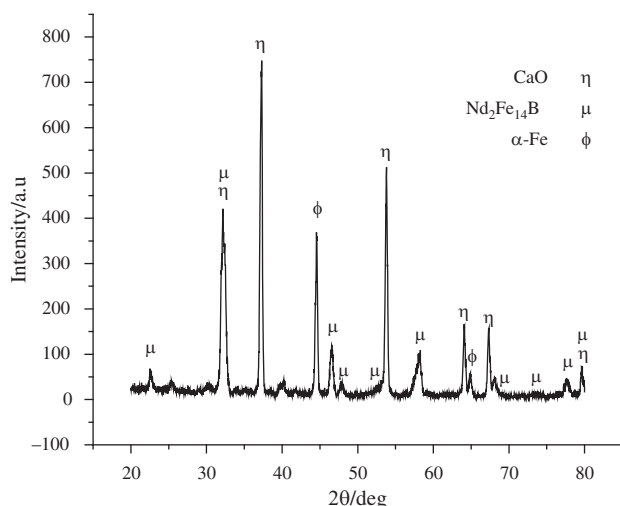


Fig. 4. The XRD pattern of unwashed product after reduction of metal oxides in vacuum at 800 °C for 2 hrs. Two magnetic phases were identified, a hard phase Nd₂Fe₁₄B and a soft phase α -Fe along with a byproduct CaO as third phase in the pattern.

Heat treatment of the Nd-Fe-B gel at 400 °C in air resulted in the formation of intermediate phases of NdBO₃, FeBO₃ and Fe₂O₃ as shown by X-ray diffraction pattern in Figure 2. Annealing of the Nd-Fe-B powder at 800 °C in air resulted in the formation of metal oxide phases of Fe₂O₃, B₂O₃, Nd₂O₃ and NdFeO₃ as shown by X-ray diffraction pattern in Figure 3.

For the Nd₂Fe₁₄B phase formation, the oxide powder was mixed with CaH₂ in an Ar glove box and the mixed powder was then pelletized. The pellet was annealed in vacuum at 800 °C for 2 hrs. The resulting reaction product was a mixture of Nd₂Fe₁₄B, α -Fe and CaO as analyzed by X-ray diffraction pattern shown in Figure 4. The CaO was leached out by washing with acetic acid and

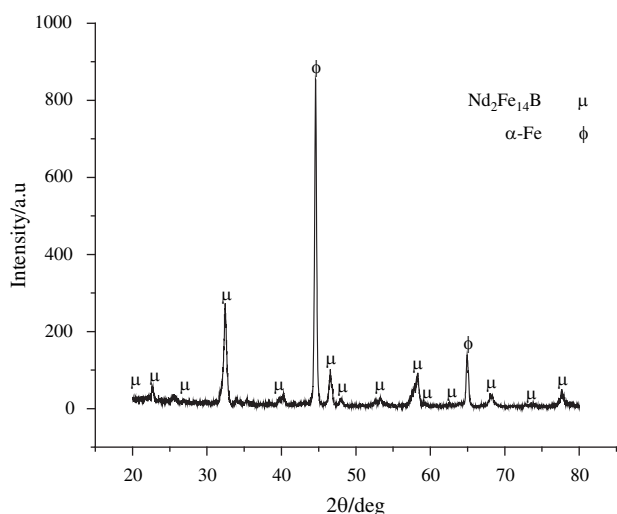


Fig. 5. The XRD pattern of washed product after reduction of metal oxides in vacuum at 800 °C for 2 hrs. Two magnetic phases were identified, a hard phase Nd₂Fe₁₄B and a soft phase α -Fe in the pattern.

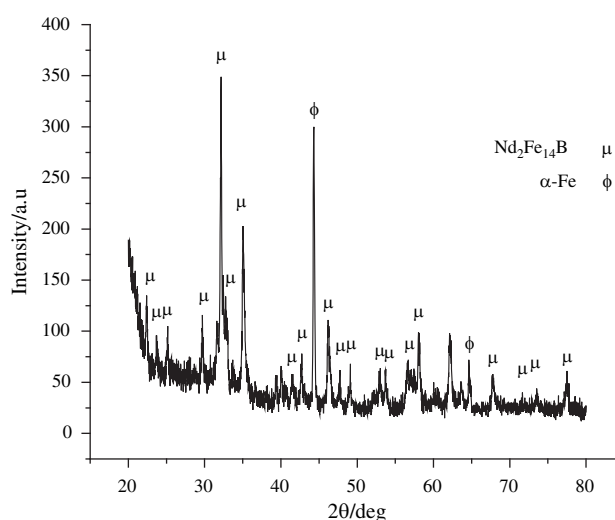


Fig. 6. The XRD pattern of washed product after reduction of metal oxides in vacuum at 920 °C for 2 hrs. Two magnetic phases were identified, a hard phase Nd₂Fe₁₄B and a soft phase α -Fe in the pattern.

deionized water. The washed product was characterized by X-ray diffraction and it was found that there exist two phases, a hard magnet Nd₂Fe₁₄B phase and a soft magnet α -Fe phase. In the X-ray diffraction pattern shown in Figure 5, Nd₂Fe₁₄B phase was compared with standard card PDF#39-0473 and the α -Fe phase was compared with the standard card PDF#06-0696. A small fractional loss of neodymium occurred during heat treatments at elevated temperatures as well as during washing process, which disturbed the nominal composition of metal ions and caused the presence of α -Fe as a separate phase. In order to obtain a large amount of stoichiometric Nd₂Fe₁₄B, a control on the Nd content in reaction steps and the washing step was needed. The Nd loss could be compensated by adding suitable amount of Nd in excess to the starting material so as

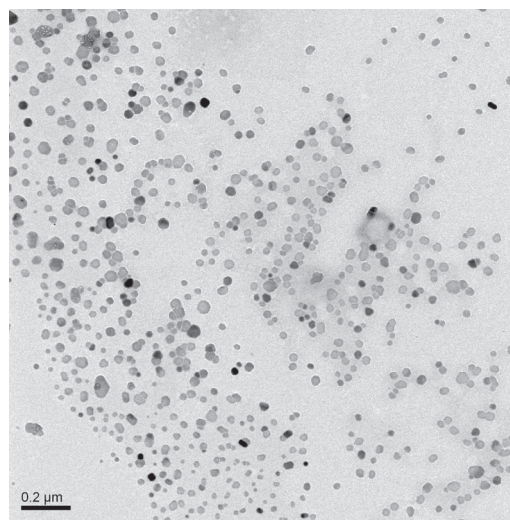


Fig. 7. TEM micrograph of the sample annealed at 920 °C for 2 hrs. This shows well scattered grains with size ranging 50–70 nm.

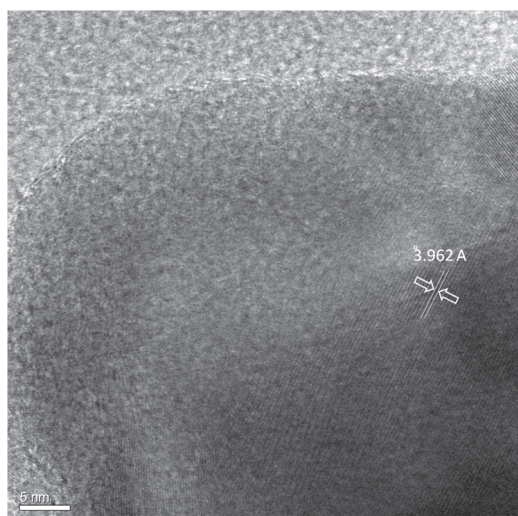


Fig. 8. HRTEM of the sample annealed at 920 °C for 2 hrs. This shows the polycrystalline nature of the sample and confirms the presence of $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase.

to ensure the maximum proportion of $\text{Nd}_2\text{Fe}_{14}\text{B}$ in final product. In order to get good crystallinity and maximum phase formation of $\text{Nd}_2\text{Fe}_{14}\text{B}$, the reduction-diffusion was carried out at 920 °C for 2 hrs in vacuum. An enhancement in crystallinity and $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase was observed as shown by X-ray diffraction pattern in Figure 6.

The TEM micrograph in Figure 7 revealed that the particles of $\text{Nd}_2\text{Fe}_{14}\text{B}$ were scattered and the synthesized powder was having an average grain size of 50–70 nm. The HRTEM image in Figure 8 indicated the polycrystalline nature of the powder. It confirmed the d -spacing of 3.9 Å for the plane (2 1 0) included in the standard pattern of $\text{Nd}_2\text{Fe}_{14}\text{B}$. The SAED results as shown in Figure 9, confirmed the diffraction planes (2 2 0), (3 0 1) and (3 3 2)

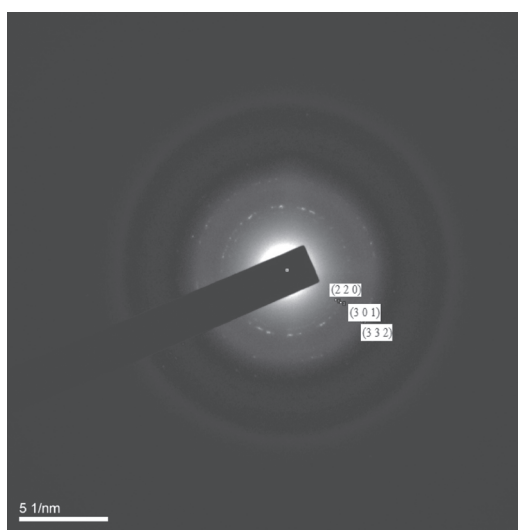
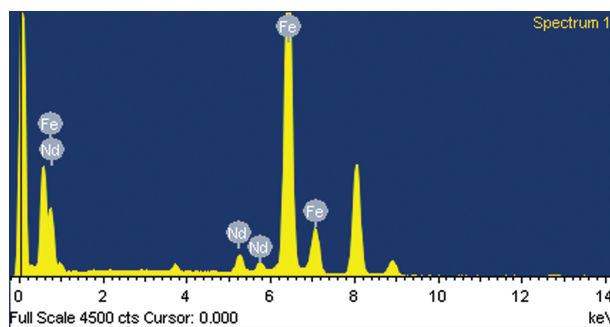


Fig. 9. SAED pattern of the sample annealed at 920 °C for 2 hrs. This shows the polycrystalline nature of the sample and gives the diffracting planes, all included in the standard diffraction pattern of $\text{Nd}_2\text{Fe}_{14}\text{B}$.



Element	Weight%	Atomic%
Fe K	88.11	95.03
Nd L	11.89	4.97
Totals	100.00	

Fig. 10. EDS of the sample annealed at 920 °C for 2 hrs. This confirms the presence of Nd and Fe and the Boron being light element remained undetected.

and (3 3 2) of the standard $\text{Nd}_2\text{Fe}_{14}\text{B}$ pattern. The EDS measurements as shown in Figure 10 detected the Nd and Fe whereas B being a light element remained undetected. This study revealed that the pechini type sol-gel synthesis method followed by reduction-diffusion of the mixed oxides provides the uniform distribution of metal ions in the synthesis route and permits lower formation temperatures for the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase. This method can effectively be used to synthesize Nd-Fe-B in nanoparticle form which leads to exchange coupled permanent magnets with enhanced energy product.

The hysteresis loop shown in Figure 11 represented the magnetic characteristic curve of washed sample of Nd_2

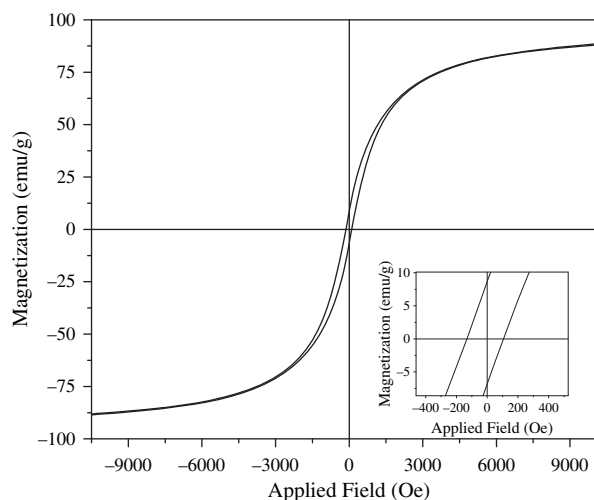


Fig. 11. Hysteresis loop of the sample annealed at 920 °C for 2 hrs.

Fe₁₄B/ α -Fe powder obtained after reduction. It was observed that the washed powder caused a saturation magnetization of 88.83 emu/g and remnant magnetization of 8.89 emu/g. The coercivity of the washed powder was $H_c = 133.89$ Oe. This was obviously soft phase magnetic behavior due to superparamagneticity of nanoparticles less than 80 nm diameter. The magnetic properties of the Nd₂Fe₁₄B/ α -Fe nanopowder studied in the present work were strongly resultant from magnetization degrading factors like washing treatments and expected agglomeration. To overcome these problems one should avoid the usage of nonmagnetic and washable reducing agent like CaH₂. Reduction of metal oxides may be carried out employing some reducing gases such as H₂, by optimizing the parameters of temperature and pressure of environment of argon or nitrogen.

4. CONCLUSIONS

The reduction and diffusion process has widely been used to fabricate ferromagnetic materials by physical as well as soft chemistry methods. To avoid the requirement of high cost pure metal precursors and additional processing energy, pechini type sol–gel method has been suggested to obtain the required metallic compounds. The Nd₂Fe₁₄B/ α -Fe nanoparticles were prepared using the pechini type sol–gel method followed by the process of solid state reduction-diffusion. This work shows that Nd–Fe–B based alloys can successfully be obtained by reduction of a mixed metal oxides system. The phase formation, size and shape of the nanomagnetic particles were determined by X-ray diffraction technique, TEM and PPMS respectively. The gel of Nd–Fe–B was prepared from the corresponding salts of Nd, Fe and B by using citric acid and ethylene glycol as the gelating agent. Annealing of the gel at 800 °C resulted in the formation of the Nd₂O₃, NdFeO₃, Fe₂O₃ and B₂O₃. The process of reduction-diffusion of the oxides complex gave a desired mixture of Nd₂Fe₁₄B phase and α -Fe.

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References and Notes

1. J. M. D. Coey and J. M. Magn, *Mater.* 226, 2107 (2001).
2. Y. S. Kang and D. K. Lee, *Int. J. Nanosci.* 5, 315 (2006).
3. Y. Li, Y. B. Kim, M. J. Kim, M. S. Song, J. H. Yong, T. K. Kim, and C. O. Kim, *J. Mater. Sci. Technol.* 16, 129 (2000).
4. T. W. Hyeon, *Chem. Comm.* 927 (2003).
5. A. H. Lu, E. L. Salabas, and F. Schuth, *Angew. Chem. Int. Edit.* 46, 1222 (2007).
6. N. A. Frey, S. Peng, K. Cheng, and S. Sun, *Chem. Soc. Rev.* 38, 2532 (2009).
7. I. Zasada, *J. Nanosci. Nanotechnol.* 11, 210 (2011).
8. H. Zhang, S. Peng, C. B. Rong, J. P. Liu, Y. Zhang, M. J. Kramer and S. Sun, *J. Mater. Chem.* 21, 16873 (2011).
9. E. F. Kneller and Hawig, *IEEE Trans. Magn.* 27, 4 (1991).
10. J. Y. Hwang, J. S. Park, H. I. Yim, T. W. Kim, D. Y. Shin, and S. B. Lee, *J. Nanosci. Nanotechnol.* 11, 856 (2011).
11. A. M. Belemuk and S. T. Chui, *J. Appl. Phys.* 110, 073918 (2011).
12. C. N. Chinnasamy, J. Y. Huang, L. H. Lewis, B. Latha, C. Vittoria, and V. G. Harris, *Appl. Phys. Lett.* 93, 032505 (2008).
13. H. Zhang, S. Peng, C. B. Rong, J. P. Liu, Y. Zhang, M. J. Kramer and S. Sun, *J. Mater. Chem.* 10.1039/c1jm11753j (2011).
14. L. Haiming and M. Xiangkang, *J. Nanosci. Nanotechnol.* 10, 7498 (2010).
15. C. Bozea, I. I. P. Blandino, and K. Robbie, *Biointerphases* 2, 17 (2007).
16. Nanostructures and Nanomaterials, Synthesis, Properties and Applications 2nd Edn., World Scientific Publishing, Singapore (2004).
17. W. Wu, Q. He, and C. Jiang, *Nanoscale Res. Lett.* 3, 397 (2008), DOI:10.1007/s11671-008-9174-9.
18. C. W. Kim, Y. H. Kim, H. G. Cha, and Y. S. Kang, *Phys. Scripta* T129, 321 (2007).
19. Y. Haik, J. Chatterjee, and C. J. Chen, *J. Nanopart Res.* 7, 675 (2005).
20. H. G. Cha, Y. H. Kim, C. W. Kim, and Y. S. Kang, *IEEE Trans. Magn. NMDC*, 1, 656 (2006).
21. P. K. Deheri, V. Swaminathan, S. D. Bhame, Z. Liu, and R. V. Ramanujan, *Chem. Mater.* 22, 6509 (2010).
22. S. D. Bhame, V. Swaminathan, P. K. Deheri, and R. V. Ramanujan, *Adv. Sci. Lett.* 3, 174 (2010).
23. P. K. Deheri, S. Shukla, and R. V. Ramanujan, *J. Solid State Chem.* 186, 224 (2012).
24. G. W. Qin, W. L. Pei, Y. P. Ren, Y. Shimada, Y. Endo, M. Yamaguchi, S. Okamoto, and O. Kitakami, *J. Nanosci. Nanotechnol.* 11, 10796 (2011).
25. S. G. Kwon and T. W. Hyeon, *Acc. Chem. Res.* 41, 1696 (2008).

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