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High-coercivity ferrite magnets prepared by mechanical alloying

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Abstract

Nanocrystalline hexaferrite ($BaFe_{12}O_{19}$ or $SrFe_{12}O_{19}$) and mixed Fe,Co-ferrite ((Fe_xCo_{1-x})Fe_2O_4 with $x=0$–1) materials have been prepared by mechanical alloying and subsequent annealing. High coercivities were obtained in these nanocrystalline materials, 6–7 kOe for hexaferrite and ~3 kOe for Co-ferrite. Hexaferrite powders prepared by mechanical alloying have been used as the starting material for high-coercivity bonded magnets. Hot-pressed anisotropic hexaferrite magnets have been produced with high values of coercivity and remanence. High magnetic performance was also achieved in some mixed Fe,Co-ferrites after magnetic annealing.

Keywords: Ferrite magnets; Hexaferrite; Mechanical alloying

1. Introduction

Permanent magnet materials have found many applications in a wide variety of areas [1]. Ferrite-based magnetic materials, especially $BaFe_{12}O_{19}$ and $SrFe_{12}O_{19}$, are still the most widely used starting materials as permanent magnets. They have excellent chemical stability and are relatively cheap to produce [1,2]. Ferrite magnetic materials with high coercivity also have applications as magnetic recording media [3].

High values of coercivity may be achieved in nanocrystalline materials with a grain size close to single domain particle size [1,4]. Mechanical alloying is a unique method for the preparation of materials in nanoparticulate form [5,6]. High coercivities have been reported for intermetallic materials based on rare-earth transition-metal compounds [6,7]. More recently, $BaFe_{12}O_{19}$ and $SrFe_{12}O_{19}$ have been fabricated by mechanical alloying [4,8,9]. These nanocrystalline materials exhibit much higher coercivities in comparison with hexaferrites prepared using conventional powder metallurgical processes [1,2]. High magnetic performance has also been reported for Co-ferrite materials prepared by mechanical alloying [10].

In our previous work, stoichiometric proportions of $BaCO_3+6Fe_2O_3$ and $SrCO_3+6Fe_2O_3$ were used as starting materials for mechanical alloying. A small quantity of hematite (Fe_2O_3) was present after formation of the hexaferrite phases, $BaFe_{12}O_{19}$ and $SrFe_{12}O_{19}$. The presence of the antiferromagnetic Fe_2O_3 phase led to a reduction of magnetisation. In the present work, we used excess of $BaCO_3$ and $SrCO_3$ to ensure that a single hexaferrite phase was formed. Isotropic and anisotropic $BaFe_{12}O_{19}$ and $SrFe_{12}O_{19}$ magnets have been fabricated by bonding and hot-pressing, respectively. The results of investigations of the dependence on composition, heat treatment and magnetic annealing of the magnetic properties of Co-ferrite are also presented here.

2. Experimental details

For the synthesis of $BaFe_{12}O_{19}$ and $SrFe_{12}O_{19}$, a mixture of Fe_2O_3 (99% purity) and $BaCO_3$ and $SrCO_3$ (99%), respectively, with compositions $1.1BaCO_3$ (or $SrCO_3$)$+6Fe_2O_3$ were used. For Co-ferrite, Fe_3O_4 and Co_3O_4 (99% for both) powders with a nominal composition of (Fe_xCo_{1-x})Fe_2O_4 with $x=0$–1 were mechanically alloyed. Mechanical alloying was carried out in a hardened steel vial together with ten 12 mm steel balls for 24 h using a Spex 8000 mixer/mill. A ball to powder mass charge ratio of 10:1 was chosen. For $BaFe_{12}O_{19}$ and $SrFe_{12}O_{19}$, all powder handling, milling and subsequent pressing and heat treatments were performed in air. For Co-ferrite, loading of powders was performed in a pure argon gas filled glove box.

The as-milled powders were cold pressed into cylindri-

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cal specimens of diameter 5 mm and length about 3 mm. The density after pressing was in the range of 3.5–4.0 g cm^{-3} (65–75% of the theoretical density). The heat treatments, for $BaFe_{12}O_{19}$ and $SrFe_{12}O_{19}$, were carried out for 1 h at temperatures between 600 and 1050°C in air.

$BaFe_{12}O_{19}$ and $SrFe_{12}O_{19}$ powders after annealing at 900°C were used for the starting materials for epoxy resin bonding. Epoxy resin (5 wt.%) and powder were mixed and subsequently cold pressed into cylindrical specimens with a diameter of 5 mm.

Anisotropic $BaFe_{12}O_{19}$ and $SrFe_{12}O_{19}$ samples were prepared by hot-pressing. The as-milled powder was firstly cold pressed into 5 mm diameter cylinders with a length of 4–5 mm and a density of 3–3.5 g cm^{-3}. Cold-pressed cylinders were sealed in steel tubes and hot pressed at 900°C for 1 h, with a pressure of about 200 MPa in an Instron 1126 Uniaxial tensile tester.

For Co-ferrite, the as-milled powders of $(Fe_xCo_{1-x})Fe_2O_4$ were annealed at 750°C for 1 h. For samples with $x \leq 0.6$, the heat treatment was performed in vacuo. The samples with $x = 0.7–1$ were annealed in air. After annealing the samples were maintained for 2 h at 200°C in air. Magnetic annealing was carried out at 300°C in vacuo in a magnetic field of 10 kOe.

The samples were examined using X-ray diffraction (Siemens D5000 diffractometer with Cu Kα radiation) and ^{57}Fe-Mössbauer spectroscopy (Canberra Packard). The magnetic properties were measured at room temperature using an Oxford Instruments vibrating sample magnetometer with a maximum applied field of 50 kOe. The hot-pressed cylinders were measured both parallel and perpendicular to the direction of pressing.

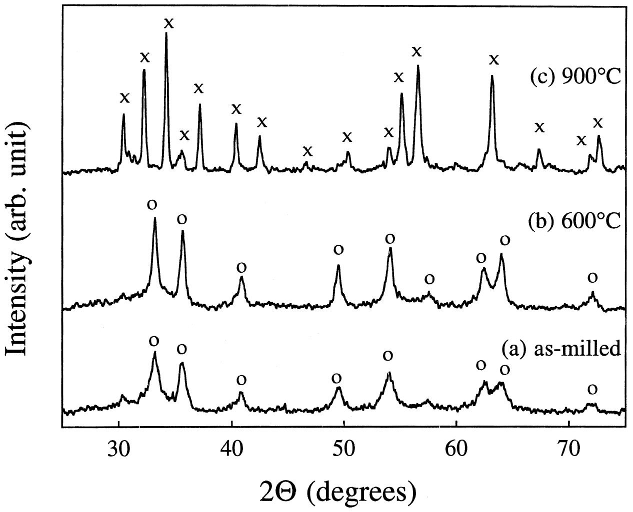

Fig. 1. X-ray diffraction patterns of $1.1BaCO_3+6Fe_2O_3$ in the (a) as-milled state and after subsequent annealing at (b) 600 and (c) 900°C ((×) diffraction peaks associated with $BaFe_{12}O_{19}$; (○) with Fe_2O_3).

3. Results and discussion

3.1. $BaFe_{12}O_{19}$ and $SrFe_{12}O_{19}$

Fig. 1 shows the X-ray diffraction patterns of $1.1BaCO_3+6Fe_2O_3$ after mechanical alloying and after subsequent annealing at 600 and 900°C, respectively. Broadened peaks associated with the hematite Fe_2O_3 phase were found in the X-ray diffraction patterns of the as-milled powders. The peaks for hematite became sharper after annealing at 600°C. The hexaferrite phase first appears after annealing at 800°C. Materials consisting of single hexaferrite phase were found after annealing at and above 850°C. These results are similar to those reported previously [4,8,9].

Room temperature Mössbauer spectra of as-milled and subsequently annealed $1.1BaCO_3+6Fe_2O_3$ are shown in Fig. 2. The as-milled powder has a spectrum consisting of two components, a non-magnetic doublet and a magnetic sextet. The magnetic sextet has a hyperfine field and other parameters which are identical to those of hematite (Fe_2O_3). The non-magnetic doublet was probably due to superparamagnetism resulting from the nanocrystalline structure or due to the presence of an amorphous phase consisting of Fe_2O_3 and $BaCO_3$ [4,8,9]. The sample annealed at 600°C consisted of hematite, and the non-magnetic doublet is not observed (Fig. 2). The disappearance of the non-magnetic doublet was probably due to growth of crystallite size or due to transformation of the amorphous phase into hematite. Samples after annealing at 900°C consisted of the single hexaferrite phase. It appears that the formation of the single hexaferrite phase is facilitated by having a small excess of $BaCO_3$ in the

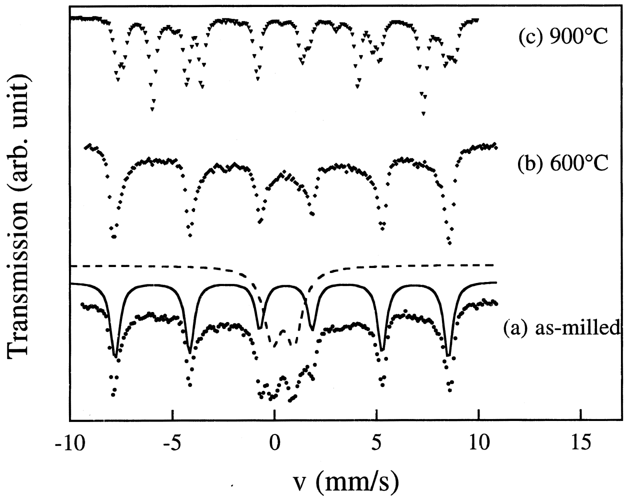

Fig. 2. Room temperature Mössbauer spectra of $1.1BaCO_3+6Fe_2O_3$ in (a) the as-milled state and after subsequent annealing at (b) 600 and (c) 900°C. The predicted hematite sextet and the non-magnetic doublet referred to in the text are shown as full and dashed lines, respectively.

starting material. When stoichiometric ($BaCO_3+6Fe_2O_3$) is used the product material contains a small amount of hematite, probably due to contamination with Fe from the steel vial and balls [4,8].

Saturation magnetisation, M_s, and coercivity, H_c, as functions of annealing temperature, T_a, are plotted in Fig. 3. The saturation magnetisation, M_s, measured at the maximum field of 50 kOe was low for the as-milled sample and the samples resulting from annealing at temperatures below 600°C. This is consistent with the results of X-ray and Mössbauer measurements which show that these samples consist of antiferromagnetic hematite. The formation of the ferrimagnetic hexaferrite phase begins at annealing temperatures around 750–800°C and accounts for the rapid increase in saturation magnetisation at these annealing temperatures (Fig. 3).

The saturation magnetisation values of samples annealed at 850–900°C were 65 and 68 emu g^{-1} which are lower than the reported saturation magnetisation of 71 and 74 emu g^{-1} for $BaFe_{12}O_{19}$ and $SrFe_{12}O_{19}$, respectively [1,2]. It has been reported previously that the saturation magnetisation of ultrafine particles of $BaFe_{12}O_{19}$ is smaller than that of the bulk material, probably due to surface effects [1,3]. When samples are heat treated at temperatures in the range 1000–1050°C the particle size increases, the surface to volume ratio decreases and the saturation magnetisation increases to a value characteristic of the bulk material.

Samples annealed at 800–900°C have high values of coercivity, 5–6 kOe for $BaFe_{12}O_{19}$ and 6–7 kOe for $SrFe_{12}O_{19}$, respectively (Fig. 3), which are similar to those reported previously for mechanically alloyed hexaferrite materials [4,8,9]. The high values of coercivity are certainly associated with the microstructure. Samples annealed at 800°C had a nanocrystalline structure, with typical crystallite sizes of ~100 nm [4]. The coercivity decreases with increasing annealing temperature, as shown in Fig. 3. Annealing at higher temperatures led to increase of the crystallite size. A typical crystallite size of ~300 nm was observed for samples annealed at 1000°C. High coercivities have also been reported for nanocrystalline hexaferrite material prepared by other methods [1,4].

The mechanically alloyed hexaferrite powders, annealed at 900°C, were formed into isotropic bonded and hot pressed anisotropic magnets and their properties were measured. The isotropic bonded magnets were fabricated from powders mixed with 5 wt.% of epoxy resin and compacted under hydraulic pressure to form cylindrical samples. The hysteresis loop of the $SrFe_{12}O_{19}$ magnet is shown in Fig. 4. $BaFe_{12}O_{19}$ and $SrFe_{12}O_{19}$ magnets had coercivities of 5.5 and 6.8 kOe, respectively. The maximum energy product was 1 MGOe which is very close to the theoretically expected maximum energy product for isotropic hexaferrite magnets [1]. The observed coercivities of these magnets (5–7 kOe) are significantly greater than the coercivities of hexaferrite materials prepared by conventional means (2–3 kOe) [1,2] which, in some applications, may be of advantage.

Anisotropic hexaferrite magnets are prepared conventionally by magnetic field alignment of the grains before sintering [1,2]. The maximum energy product $(BH)_{max}$ of these magnets is ~4 MGOe. In the present investigation anisotropic magnets were fabricated by hot pressing [1,8] the mechanically alloyed powders described above. The densities of the magnets were greater than 95% of the theoretical density of 5.3 and 5.1 g cm^{-3} for $BaFe_{12}O_{19}$ and $SrFe_{12}O_{19}$, respectively. The hysteresis loop of an anisotropic $SrFe_{12}O_{19}$ magnet is shown in Fig. 5. Coercivities in the range 5.0–5.5 kOe were observed and the remanent magnetisations were ~3.6 kG, about 80% of saturation magnetisation. The values of $(BH)_{max}$ for these anisotropic materials were in the range 2.5–3.0 MGOe which is significantly smaller than the values, noted above, obtained with magnetically aligned material. Again, anisotropic magnets prepared from mechanically alloyed materi-

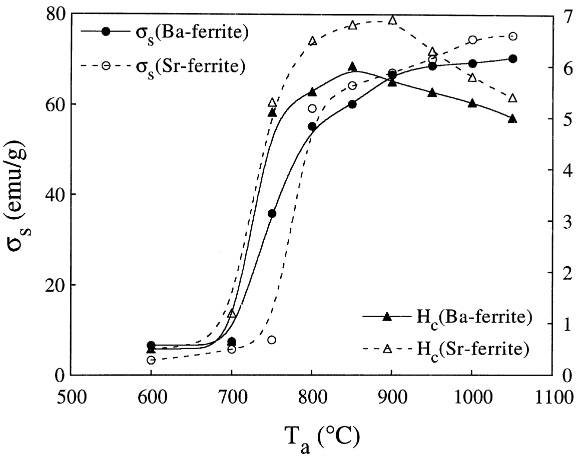

Fig. 3. Coercivity, H_c, and saturation magnetisation, σ_s, as a function of the annealing temperature, T_a, for Ba- and Sr-ferrite.

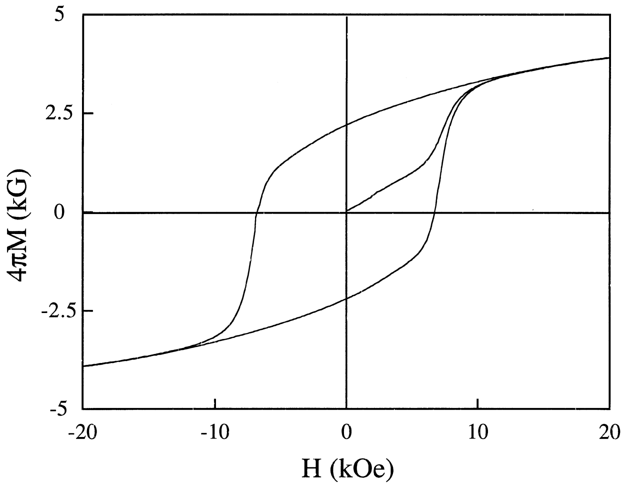

Fig. 4. Hysteresis loops of bonded Sr-hexaferrite magnet. $4\pi M_s=4.3$ kG, $4\pi M_r=2.2$ kG, $H_c=6.9$ kOe, $(BH)_{max}=1.0$ MGOe.

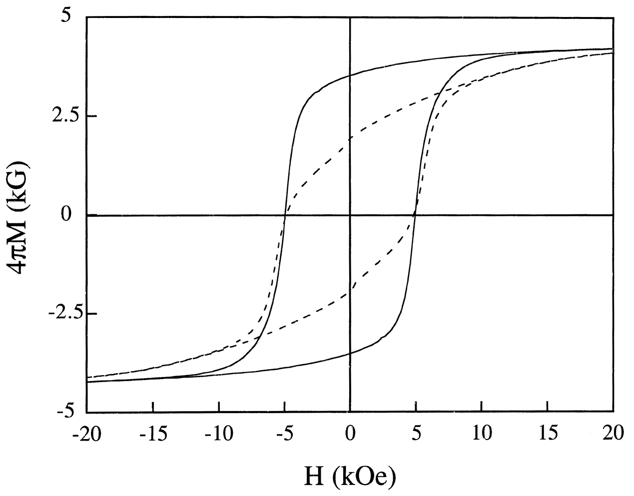

Fig. 5. Hysteresis loops of a hot-pressed Sr-ferrite magnet in the directions parallel (———) and perpendicular (- - -) to the pressing direction. $4\pi M_s=4.4$ kG, $4\pi M_r=3.6$ kG, $H_c=5.1$ kOe, $(BH)_{max}=2.8$ MGOe.

als have coercivities of 5–5.5 kOe, i.e. more than twice the coercivity of anisotropic hexaferrite magnets prepared by conventional means.

3.2. $(Fe_xCo_{1-x})Fe_2O_4$

Mixed Fe,Co-ferrites of composition $(Fe_xCo_{1-x})Fe_2O_4$ may have possible applications as permanent magnets and recording media [2,11]. In this work, we describe the properties of materials of $(Fe_xCo_{1-x})Fe_2O_4$ with $x=0$–1 prepared by mechanical alloying and subsequent annealing.

All the mechanically alloyed powders had disordered structures, evidenced by line broadening observed in X-ray diffraction and Mössbauer studies [10]. The ordered ferrite phase was obtained after annealing at 700–800°C [10]. In this work, all samples were annealed at 750°C for 1 h. For $x\leq0.6$, hematite phase (Fe_2O_3) was present after annealing at 700–800°C in air. The formation of α-Fe_2O_3 was avoided by in vacuo annealing of the samples with compositions corresponding to $x\leq0.6$. For compositions $x\geq0.7$ in vacuo annealing gave rise to the presence of wustite (FeO) which was prevented by adopting the procedure of annealing samples, with compositions corresponding to $x\geq0.7$, in air at 750°C.

Samples with compositions corresponding to $x\leq0.6$, after vacuum annealing at 750°C had relatively low coercivities. The coercivity was increased by further heat treatment at a lower temperature of 200–300°C for 1–2 h in air. As an example it was found that the coercivity of a sample of composition $(Fe_{0.5}Co_{0.5})Fe_2O_4$ increased from 1 to 2.2 kOe after additional heat treatment at 200°C for 2 h in air. No significant changes in structure and saturation magnetisation were found after the additional heat treatment. The increase of coercivity is probably due to increase of magnetic anisotropy energy [10–13]. Post-annealing heat treatment at 200°C of samples with compositions corresponding to $x\geq0.7$ produced no significant changes in magnetic properties.

The saturation magnetisation and coercivity, after annealing and optimum low temperature heat treatment, are plotted in Fig. 6 as functions of the composition variable, x. The values of saturation magnetisation of 87 and 77 emu g^{-1} for $FeFe_2O_4$ and $CoFe_2O_4$, respectively, are close to the accepted values for the two compositions [10,11]. Samples of composition corresponding to $0\leq x<0.4$ have relatively low values of coercivity, being one-third of the coercivity of samples with composition parameters in the range of $0.5\leq x\leq1$.

The grain size of Co-ferrite samples annealed at 750°C was estimated to be ~25 nm from measurements of the widths of X-ray diffraction peaks and also from electron diffraction images [10]. It has been shown that the application of a magnetic field to a mixed Fe–Co ferrite maintained at temperatures ~300°C, where significant ionic diffusion occurs, results in directional ordering of Co^{2+} ions and directional magnetic anisotropy [11] (the procedure is known as magnetic annealing). Mechanically alloyed ferrites with compositions in the range $0.5\leq x\leq1$ were subjected to magnetic annealing at 300°C. The induced anisotropy was determined by measurement of remanent magnetisation, when the measuring field was applied in the same direction as the field for magnetic annealing, and the values of coercivity were determined for measuring fields parallel and perpendicular to the magnetic annealing field direction. The results are plotted in Fig. 7.

For $CoFe_2O_4$, no significant changes in remanence and coercivity were observed after magnetic annealing since directional ordering of ions resulting in magnetic anisotropy is not possible when the B site divalent ion locations are all occupied by Co^{2+} ions. For other samples with $x=0.5$–0.8, high remanence of 70–80% of the saturation

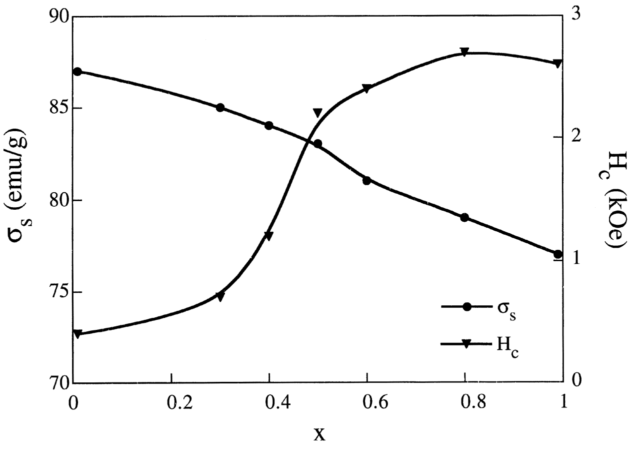

Fig. 6. Coercivity, H_c, and saturation magnetisation, σ_s, as a function of composition, x, for $(Fe_{1-x}Co_x)Fe_2O_4$ after optimised annealing.

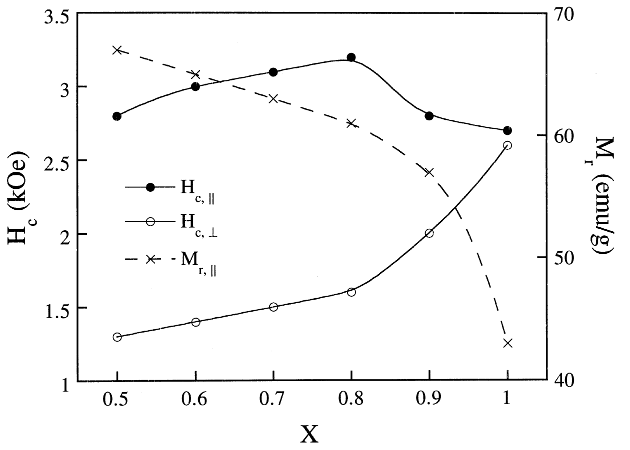

Fig. 7. Coercivity, H_c, measured in the direction parallel to the direction of magnetic field applied during the magnetic annealing (‖) and in the perpendicular direction (⊥) and remanence, σ_r, measure in the parallel direction.

magnetisation was obtained in the direction parallel to the magnetic field applied during the magnetic annealing.

For $x=0.5$–0.8, the coercivities in the parallel direction were in the range 2.8–3.2 kOe. Coercivities measured in fields acting perpendicular to the direction of the field applied during magnetic annealing ranged from 1.3 to 1.6 kOe.

High values of remanence were obtained for samples with $x=0.5$–0.8 (Fig. 7). Using values of the theoretical density, the maximum energy product was calculated to be 3–4 MGOe. These values of coercivity and maximum energy product are comparable with those obtained by commercial Ba- and Sr-hexaferrite magnets.

4. Conclusions

Barium and strontium hexaferrites have been prepared as nanocrystals by mechanical alloying. Isotropic bonded magnets fabricated from these materials have energy products $(BH)_{max}$~1 MGOe and coercivities of 5.5 and 6.8 kOe for barium- and strontium-hexaferrites, respectively. Anisotropic magnets have been produced by hot pressing. Values of $(BH)_{max}$ in the range 2.5–3.0 MGOe and coercivities of 5–5.5 kOe have been achieved.

Anisotropic mixed ferrites of composition $(Fe_xCo_{1-x})Fe_2O_4$ have been prepared by magnetic annealing of nanocrystalline powders prepared by mechanical alloying. Magnets with values of remanent magnetisation of 70–80% of saturation magnetisation, coercivities above 3 kOe and $(BH)_{max}$ products in the range 3–4 MGOe have been fabricated from these powders.

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