



Giant coercivity of dense nanostructured spark plasma sintered barium hexaferrite

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1 Introduction

- Features of current hard magnets
- RE substitutions in hexaferrites
- Nanostructured hexaferrites

2 Synthesis of Ba nano-ferrite

- Sol-gel
- Thermal treatment

3 Results

- X ray diffraction
- electronic microscopy
- Magnetic properties

4 Conclusion



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SmCo Magnets

- High coercivity; high Curie point
- Medium remanence; high cost



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Hexaferrite

- Medium coercivity; low remanence
- Positive thermal coefficient of coercivity; low cost



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La and Co substitution in Sr ferrite

Composition

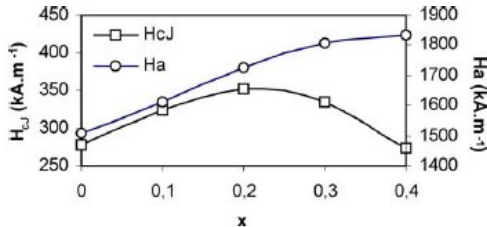
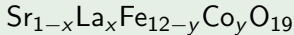


Fig. 1. Anisotropy field H_a and intrinsic coercivity H_{cJ} of $\text{Sr}_{1-x}\text{La}_x\text{Fe}_{12-y}\text{Co}_y\text{O}_{19}$ ferrite magnets measured at room temperature.

Tenaud et al., J. Alloys Comp 370 (2004)



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Néel or Stoner-Wohlfarth model

- perfectly oriented isotropic magnet

$$\mu_0 H_C = \frac{2K}{J_S} = \mu_0 H_K = 1.7 \text{ T}$$

- isotropic magnet $\mu_0 H_C = 0.48 \mu_0 H_K = 0.85 \text{ T}$ and $J_R = J_S/2 = 0.25 \text{ T}$



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Problem

- works not badly loose **nano-powders** $\mu_0 H_C \gtrsim 0.55 \text{ T}$
- sintering yields grain growth** \Rightarrow nucleation field

$$\mu_0 H_C = \mu_0 H_N = 4\mu_0 \frac{\sqrt{AK}}{J_S D} \approx 0.25 \text{ T}$$



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Solution

Use spark plasma sintering to densify without grain growth



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sol-gel citrate precursor method

starting material

- High purity iron(III) nitrate + barium hydroxide;
- citric acid → molar ratio of citrate to metal ions 2:1.;



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- iron(III) hydroxide dissolved in citric acid at 60-70°C
- barium hydroxide additon
- chelation of metal ions at pH6



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Compound formation



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- evaporation (80-90°C) + drying (150-170°C)



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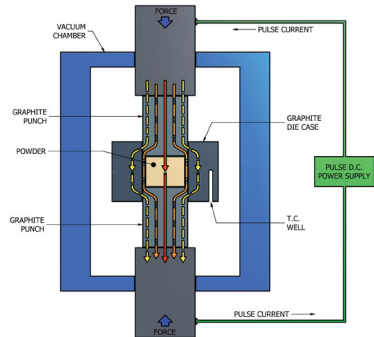
Compound formation

- evaporation (80-90°C) + drying (150-170°C)
- elimination of organic matter at 450°C for 2 hours in air
- calcination in air at different temperatures between 700 and 1000°C
- choice of optimal treatment for smaller grain size fully formed compound \Rightarrow **900°C/1 h**



Spark Plasma Sintering

- Heating rate 160 Kmin^{-1}
- Temperature **800°C**
- Duration 0 to 20 min
- Cooling rate 160 Kmin^{-1}
- Pressure 50 MPa



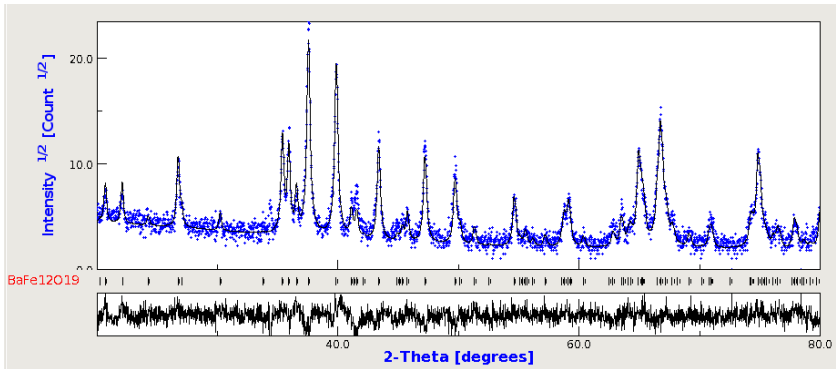
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Refinement of XRD spectra

- M phase Ba hexaferrite is formed after calcination
- example: sample SPS0 (0 min)



Computation made using Rieveld based MAUD software

Quantitative results of XRD analysis

Sample	Sintering time (min)	Lattice constants			Cr. size D (nm)	Density (%)
		a (nm)	c (nm)	v (nm ³)		
Lit*	single cryst.	0.5892	2.3183	0.6970	–	100
Com [†]	coarse grain	0.5893	2.3201	0.6977	>1000	>95
CP	as calcinated	0.5895	2.3219	0.6987	60	–
SPS0	0	0.5888	2.3238	0.6976	70	76
SPS5	5	0.5890	2.3237	0.6981	84	94
SPS13	13	0.5886	2.3222	0.6967	74	88
SPS20	20	0.5889	2.3226	0.6976	77	86

* litterature values from data base



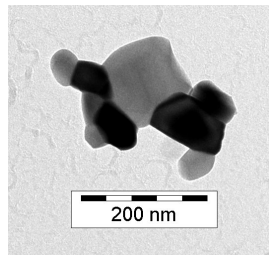
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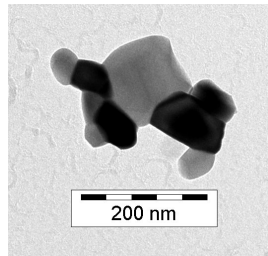
TEM — Calcinated powder

Particles are nearly equiax with size matching XRD analysis with relatively large distribution (50-200 nm)



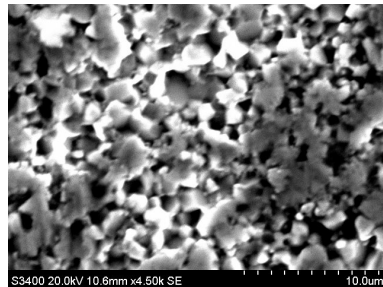
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SEM — Sintered

The material is composed of $1\mu\text{m}$ nano-grains with several 100 nm pores

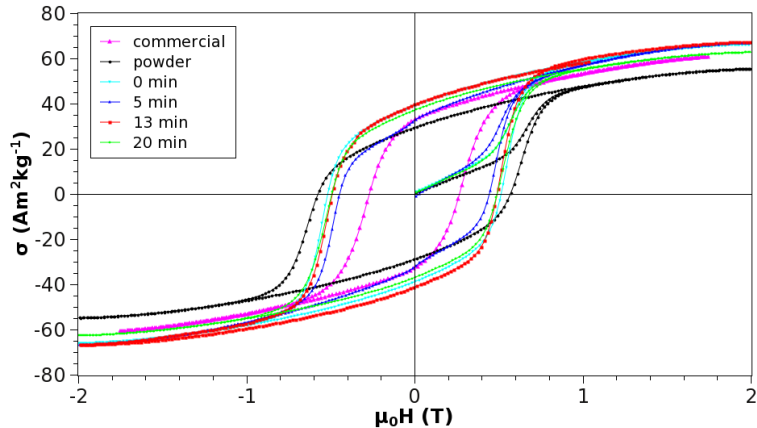


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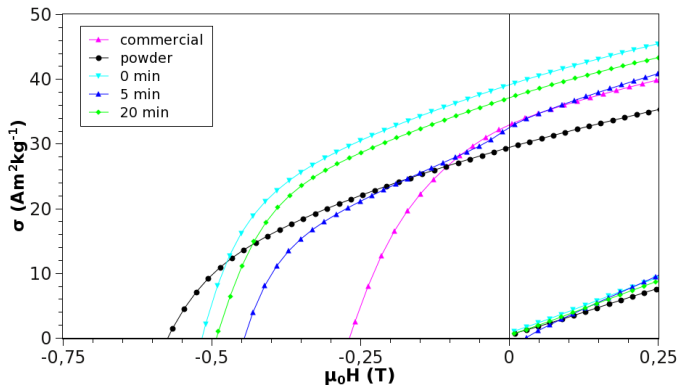
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Hysteresis loops



The role of grain size homogeneity



The double-phase behavior of sample SPS5 is due to the presence of big particles



Correlation coercivity/structure

Grain size

No clear correlation is found with the grain size, due its small change and accuracy



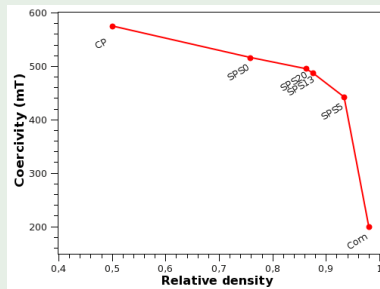
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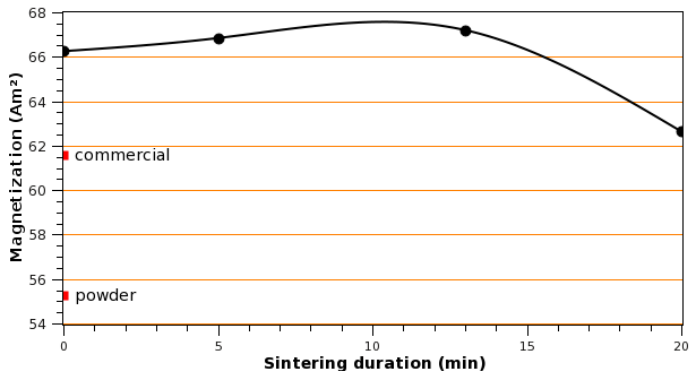
Density

Density seems to play the leading role through exchange at interface and internal demagnetization. For the powder (CP) d is arbitrarily set to 0.5

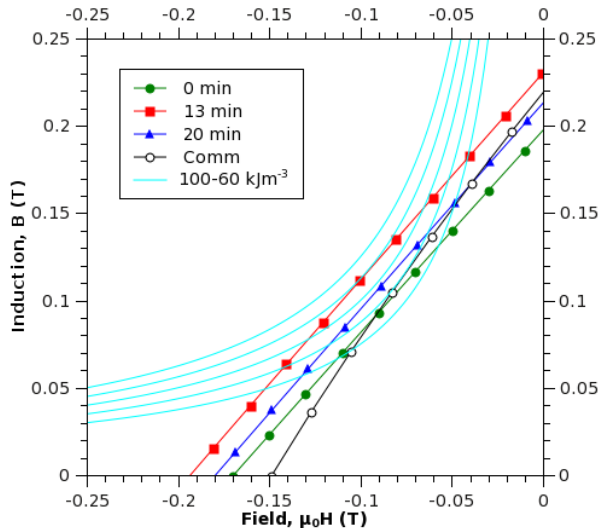


Saturation magnetization

- ① sintering presumably changes Fe^{3+} positions in the different sites $\Rightarrow M_S \nearrow$ (lattice parameter $c \nearrow$)
- ② reduction of Fe^{3+} into $\text{Fe}^{2+} \Rightarrow M_S \searrow$



Functional properties



Conclusion and prospects

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- 1 SPS combines very fine grain size and high density



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Problem

- Orientation of nano-particles is difficult



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- EU foundation of FP7 project SSEEC # NMP-SL-2008-274864



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Thank you for your attention!

