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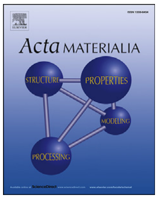

Full length article

In-situ magnetic force microscopy analysis of magnetization and demagnetization behavior in Al^{3+} substituted Sr-hexaferrite

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ABSTRACT

The sintering temperature of an Al^{3+} substituted Sr-hexaferrite composite was systematically varied from 1180 °C to 1280 °C resulting in different microstructures. The grain size was found to range from a few hundred nanometers to several hundred micrometers depending on Al content and sintering temperature. Adding an Al substituted powder to a commercial powder increased the coercivity from 360 mT to 470 mT, at the same time, decreasing remanence from 350 mT to 305 mT. Magnetization and demagnetization processes from the thermally demagnetized state (TDS) and DC-demagnetized state (DCD) have been investigated systematically by *in-situ* magnetic force microscopy (MFM) under magnetic field. From the surface domain contrast a polarization was derived which quantitatively matches the global i.e. bulk polarization obtained by superconducting quantum interface device (SQUID) magnetometry. The shape of the initial polarization curve and the polarization from the DCD state were correlated with the *in-situ* MFM data revealing a distinctly different magnetization behavior depending on grain size. The presented results enable a better understanding of local nucleation mechanisms, global influences of pinning centers and further opportunities to improve rare earth (RE) free permanent magnets based on ferrites.

1. Introduction

Due to their low price and abundance of raw materials, hexaferrites are the mostly used permanent magnets accounting for a volume of approximately 80% of the global demand per year [1,2]. In addition hexaferrites are mechanically and chemically stable, corrosion resistant, possess low electrical conductivity with a reasonably magnetic anisotropy field (H_A) and intrinsic coercivity ($_iH_c$) for low cost applications. They are therefore used in a large variety of permanent magnet applications. An enhanced coercivity $_iH_c$ can be achieved by limiting the particle size below the single domain particle size of 740 nm [3,4]. A further improvement of the magnetic performance could be achieved by the addition of cobalt and light rare earth elements like lanthanum which increases the coercivity while simultaneously increasing the remanence [5]. However, these approaches boost the raw material costs significantly. Alternatively Fe^{3+} can be substituted by Al^{3+} which leads to a higher coercivity. The reason is the increase of the magnetic anisotropy field H_A (H_A=K_1/M_s). Despite the fact that introducing Al^{3+} reduces the total number of moments per unit cell and thereby K_1 [6] it reduces M_s even stronger, resulting in an overall increased anisotropy field H_A.

Using various attempts of chemical synthesis methods, such as hydrothermal [7], sol-gel [6,8,9], co-precipitation [10–12], self-propagating reaction [13,14] or auto combustion [15,16] small particles with a diameter below 100 nm with high coercivity can be synthesized. However, by the commercial process of solid-state reaction [17,18] a high saturation magnetization M_s is achieved using high calcination temperatures up to 1300 °C which in contrast leads to a degradation of coercivity $_iH_c$ by grain coarsening. Taguchi et al. could produce small particles of approximately 300 nm in diameter with a high coercivity $_iH_c$ of 530 mT and saturation magnetization M_s of 450 mT [19]. Essential for the high coercivity is the mechanochemical activation of Fe_2O_3 and the synthesis of small raw particles (30 nm) of $SrCO_3$ by a reaction of $SrCl_2$ in a Na_2CO_3 aqueous solution before powder calcination.

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In the present work, we introduce composites from a commercial high remanent hexaferrite (M884 Tridelta) (80 wt%) and a high coercivity Al rich Sr-hexaferrite ($SrFe_{10}Al_2O_{19}$) (20 wt%). We recently published the detailed synthesis of the Al rich Sr-hexaferrite ($SrFe_{10}Al_2O_{19}$) [20]. The objective now is to enhance coercivity by the addition of the Al rich Sr-hexaferrite ($SrFe_{10}Al_2O_{19}$) phase with a high magnetic anisotropy field. In the case of hexaferrites the production of particles in the range of few hundred nanometers with high coercivity and remanence by solid-state reaction is quite difficult, especially, after the sintering process.

Domain structures at the polished surface of the hexaferrite composite magnets were analyzed for the thermally demagnetized, saturated and remanent state by magnetic force microscopy (MFM). Investigations of the domain structures during magnetization and demagnetization under external magnetic field were observed via MFM under *in-situ* conditions. In addition, the influence of Al substitution on the magnetic reversal mechanism and the correlation of the global bulk polarization (measured by SQUID-magnetometry) and the local polarization (determined from MFM contrast) were studied. The results allow a better understanding of the magnetic hardening mechanism of hexagonal ferrites and further optimisation of this material class.

2. Experimental

2.1. Synthesis

As starting materials 80 wt % commercial calcined and milled hexaferrite powder M884 (Tridelta Hartferrite GmbH, containing $CaSiO_3$ and Al_2O_3, $H_c \approx 130$ kA/m and $M_s \approx 66.5$ Am^2/kg of milled powder) was mixed with annealed $SrFe_{10}Al_2O_{19}$ powder ($H_c \approx 640$ kA/m and $M_s \approx 42$ Am^2/kg, the annealing process is described more in detail in Ref. [20]) in a polyamide grinding jar with isopropanol and agate balls. The powders were mixed with two balls with a diameter of 30 mm and five balls with a diameter of 20 mm on a roller mill for 24 h. The slurry was pressed in a commercial prototype press of Tridelta Hartferrit GmbH to a green compact with a disc diameter of 50 mm. An axial magnetic field of 0.9 T was applied in combination with a pressure of 40 kN. The green compact disc was cut in smaller pieces, which were sintered at different temperatures T_{sinter} between 1160 °C and 1280 °C for a period of 90 min. The heating rate was adjusted to achieve the sinter temperature after 6 h and followed by a cooling of 1200 K/h. Cuboids of approximately $5 \times 5 \times 3$ mm^3; were cut from the samples and used for magnetic characterization using a hystograph. In a second step these small pieces were cut in the middle (surface area of about 0.25×0.5 cm^2) for MFM and SQUID measurements. For

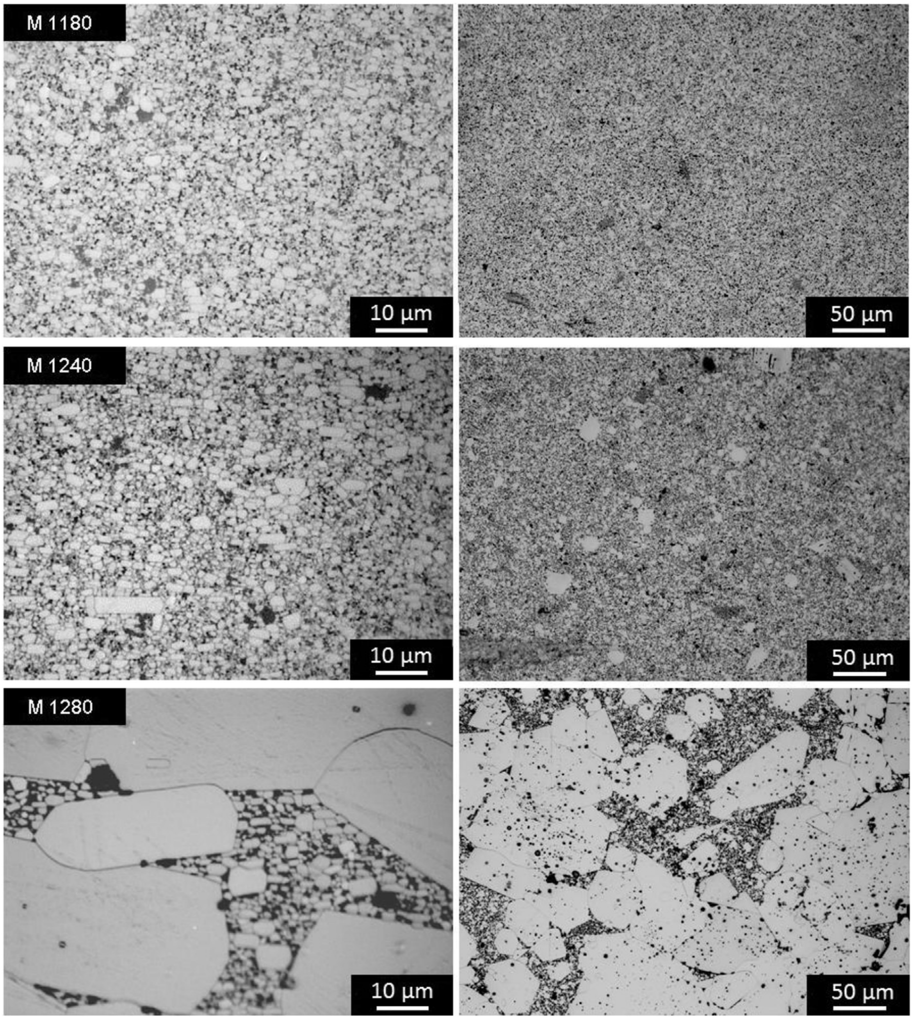

Fig. 1. Cross section (left) and top view (right) of the microstructure after sintering at 1180 °C, 1240 °C and 1280 °C of Al^{3+} substituted Sr-hexaferrite. Easy axis is perpendicular to the top view.