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Preparation and Properties of Barium-ferrite-containing Glass Ceramics

Robert Müller,* Claudia Ulbrich, Walter Schüppel, Hanna Steinmetz and Erwin Steinbeiß

Institut für Physikalische Hochtechnologie e.V., Helmholtzweg 4, D-07743 Jena, Germany

Abstract

Magnetic properties of magnetic ceramics are dependent on the magnetisation processes. They are usually dominated by Bloch-wall displacements in multi-domain structures of the sintered magnetic material, even if the starting powder material shows single-domain Stoner–Wohlfarth behaviour. Domain wall motion limits in several cases the quality of magnetic materials for special applications like permanent magnets or rf devices. We have developed a new type of magnetic powder preparation which permits the fabrication of compact glass ceramics containing Ba-ferrite maintaining the single-domain behaviour of the starting powder. This technology is based on the glass crystallisation method for the precipitation of single-domain Ba-ferrite particles in a quenched melt of Fe_2O_3–BaO–B_2O_3(-SiO_2). By milling the crystallized melt or leaching out the borate from the SiO_2-containing glass, a glass ceramic powder containing Ba-ferrite can be produced, which can be sintered at moderate temperatures providing a dense compact glass ceramic containing up to 90 wt% Ba-ferrite. This compact glass ceramic shows the same single-domain behaviour as the starting powders, i.e. it also possesses the high coercivities of hard magnetic material. © *1999 Elsevier Science Limited. All rights reserved*

Keywords: sintering, magnetic properties, ferrites, glass ceramics, hard magnets.

1 Introduction

Compact ferrites are prepared usually by sintering of ferrite powders with a mean particle size of about 1 μm at 1200–1250°C. During sintering the ferrite crystallites grow so that multi-domain behaviour (Bloch-wall displacements) occurs which lowers the coercivity of the material. The aim of our work is the preparation of a compact body in which ferrite particles are well dispersed and maintain the single domain behaviour (homogeneous magnetisation rotation, Stoner–Wohlfarth behaviour). Therefore we prepared compact glass ceramics by sintering of a pressed powder which contains single domain particles (<500 nm) separated by a nonmagnetic matrix which lowers the sinter temperature, prevents the particles from growing to multi-domain ones and causes low magnetic interaction. A further problem is the realisation of such a behaviour in a material with a ferrite content as high as possible.

*To whom correspondence should be addressed. Fax: +49-3641-302799; e-mail: robert.mueller@main.ipht-jena.de

2 Results and Discussion

2.1 Particle preparation

To produce the single domain particles separated by a matrix we have used the glass crystallization method GCM.[1] A glass in the system BaO–Fe_2O_3–B_2O_3(-SiO_2) was melted in air at ≈1400°C. Then, the melt was quenched to get amorphous flakes in which the ferrite particles precipitate during heat treatment. We chose annealing conditions leading to a maximum coercivity in the flakes indicating single domain behaviour. The particles can be isolated by dissolving the borate matrix.

The specific saturation magnetisation σ_∞, (value extrapolated for infinite field strength) and the coercivity H_C were determined with a vibrating sample magnetometer. X-ray diffraction, electron microscopy and hydrostatic weighing were carried out.

2.2 Ba-ferrite in borate matrix

First experiments[2] were done in the system 40 BaO–27 Fe_2O_3–33 B_2O_3 (mol%) which is well

known from the GCM. The amorphous flakes were first heat treated at temperatures from 780 to 820°C for 4 to 24 h which leads to crystallisation of small single-domain ferrite particles within a barium borate matrix. The flakes were ground in an agate ball mill. Thereafter the powder was pressed isostatically at 150 MPa and sintered at 850°C corresponding to the dilatometric investigations. The sintering time was only 10 min in order to avoid a further grain growth leading to multi-domain particles. Samples larger than 1 cm must be slowly heated up and cooled down to prevent cracks.

The resulting compact glass ceramics reveal sinter densities of >97% of the theoretical density. Only M-type Ba-ferrite and Ba-borate is detected by X-ray diffraction. The magnetic properties of the compact glass ceramics are comparable with those of the annealed flakes. The specific saturation magnetization of such samples lies between 26 and 28 $Am^2\ kg^{-1}$, i.e. 90–100% of the possible value corresponding to the ferrite content of 40% and assuming a bulk material value of 72 $Am^2\ kg^{-1}$.[3] The coercivities reach values above 400 kA m^{-1}.

2.3 Glass ceramics with SiO_2 matrix

For applications a glass ceramic with a ferrite content as high as possible is desirable. In order to increase the ferrite content of the annealed flakes above 50%, a high Fe_2O_3-content of the initial melt (>35 mol%) is necessary but leads to large ferrite crystals which show the full magnetization values but lower coercivities (<≈300 kA m^{-1}, see Fig. 5 below) due to multi-domain behaviour. In order to prevent the growth of the ferrite crystallites we have modified the initial melt by addition of SiO_2.

The preparation of annealed flakes was analogous to the method mentioned above. The following compositions were used: 27 Fe_2O_3–40 BaO–$(33-x)B_2O_3$–x SiO_2 with $5<x<20$ in mol% leading to a ferrite fraction between ≈95 and 81 wt%. Besides the formation of the ferrite particles a segregation of the matrix into Ba-borate and SiO_2 takes place. The borate phase was removed by dissolution in hot diluted acetic acid and the remaining material was afterwards rinsed and dried. To avoid losses of SiO_2 the slurry had to be centrifuged and freeze dried. After this step a homogeneous mixture of Ba-ferrite plate-like crystals with a preferential diameter range from 50 to 500 mm and a diameter/thickness ratio from about 5 up to 10 and much finer SiO_2-particles (diameter about 5 nm) was achieved (Fig. 1) without any additional, mechanical homogenization treatment. The Ba-ferrite crystallites are coated by the much finer SiO_2 particles.

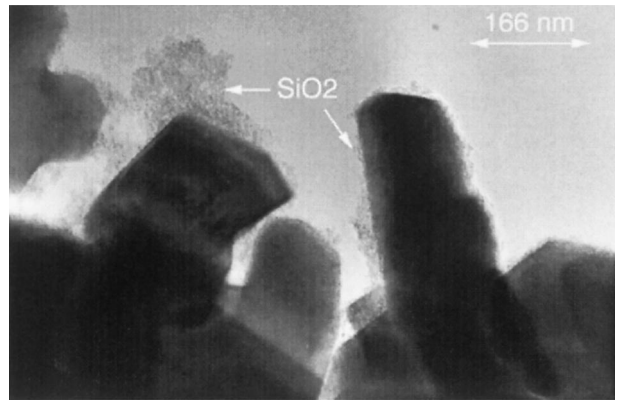

Fig. 1. TEM picture of Ba-ferrite powder coated with SiO_2 particles.

The powder mixture was isostatically pressed at 150 MPa and sintered between 980 and 1050°C corresponding to the dilatometric investigations. With increasing the sintering temperature, a strong decrease of the saturation magnetization can be observed (Fig. 2) due to a transition from $BaFe_{12}O_{19}$ to α-Fe_2O_3. To avoid this transition we chose to sinter at temperatures between 980 and 1000°C for further investigations.

The coating of the ferrite particles with SiO_2 in the powder mixture maintains the particle–particle separation of the Ba-ferrite crystallites in the glass ceramics, if the SiO_2 content is large enough. A crude estimation for the necessary SiO_2 content follows from the assumption that at least each of the Ba-ferrite platelets is covered by a surface layer of SiO_2-spheres with one half of the maximum 2D-packing density, leading to an upper limit of about 80 mass% Ba-ferrite in the glass ceramic. From Fig. 3 the separation of the particles even in particle

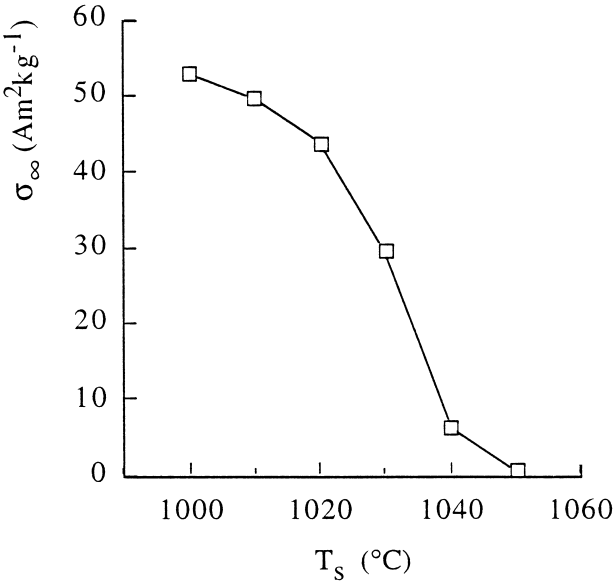

Fig. 2. Specific saturation magnetization of SiO_2-containing samples versus sinter temperature (sinter time 30 min, 20% SiO_2).

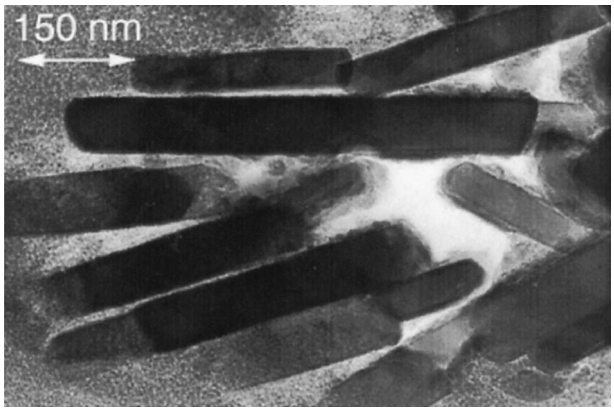

Fig. 3. TEM picture of a ferrite glass ceramic with SiO_2 matrix; the separated ferrite particles (dark) can be seen.

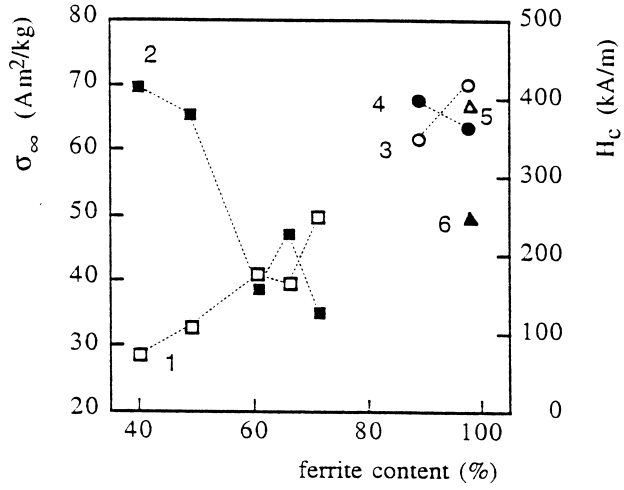

Fig. 5. Influence of the ferrite content of borate glass ceramics on (1) σ_∞ and (2) H_c, of SiO_2 glass ceramics on (3) σ_∞ and (4) H_c, of a conventional isotropic ferrite on (5) σ_∞ and (6) H_c.

stacks which are not typical for the samples can be observed. The material shows a near ordering which is different from that of a conventional powder material, which results in a different dipole–dipole interaction contribution to the magnetic ensemble properties. The magnetic behaviour of such glass ceramics can be described by a modified Stoner–Wohlfarth model.[4]

The specific saturation magnetization of the samples lies between 90 and 100% of the possible value corresponding to the ferrite content and assuming a bulk material value of $72\,Am^2\,kg^{-1}$. This is somewhat lower than the values of non-sintered powders due to a beginning of phase transition into Fe_2O_3 which is known from X-ray diffraction patterns. This transition could be avoided by optimizing the sinter conditions.

Coercivity values of sintered samples are 397 kA m^{-1} (Figs 4 and 5) if made from initial powders prepared by annealing conditions leading to a maximum coercivity ($\approx$420 kA m^{-1}) in the flakes. This value is much higher than the values of typical conventional ferrite samples[5] (Fig. 5). The decrease of the coercivity observed for the glass ceramics compared with the powder mixture, which is found for all Ba-ferrite concentrations, indicates that a continued, lateral growth of some large Ba-ferrite crystallites during sintering takes place. In the case of samples with the maximum H_c of the flakes, the size of some particles becomes too large for single-domain switching.[1] Further effort is necessary to optimize the technology with respect to the optimal particle size.

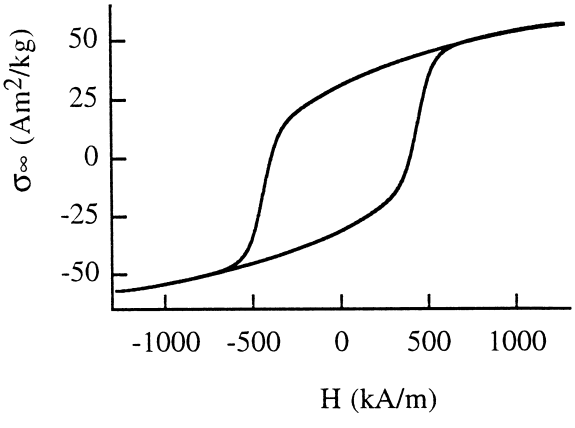

Fig. 4. Hysteresis loop of a ferrite–SiO_2 glass ceramic.

3 Conclusions

Dense, homogeneous glass ceramics with about 40 mass% Ba-ferrite as the only magnetic phase can be prepared in the system Fe_2O_3–BaO–B_2O_3 with magnetic properties comparable to single domain Ba-ferrite powder. Increasing ferrite contents up to $\approx$ 70 mass% leads in this system to a strong decrease of the coercivity.

Glass ceramics with > 90 mass% ferrite content could be prepared in the system Fe_2O_3–BaO–B_2O_3–SiO_2 by removing the borate after ferrite crystallization to single domain particles and sintering of the ferrite–SiO_2 mixture. A transition to Fe_2O_3 could be avoided by optimal sintering conditions. In this glass ceramics the single domain behaviour could nearly be maintained with coercivities $\approx$ 400 kA m^{-1}.

The SiO_2-containing glass ceramics show a much better chemical resistance compared with borate glass ceramics.

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