Research articles

Morphology and magnetic properties of pressed barium hexaferrite BaFe_{12}O_{19} materials


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A B S T R A C T

Barium hexaferrite tablets were compacted at pressures of 50–149 kN/cm² and subsequently calcined at different temperatures up to 1350 °C for various durations. The compaction pressure has a non-monotonic influence on the calcined sample density and coercivity. The apparent density shows a maximum concomitant to a minimum in coercivity near a compaction pressure of 120 kN/cm². In contrast the Curie temperature of 459 °C are not influenced by the compaction pressure. The optimized compaction pressure and subsequent calcination temperature for obtaining high-density single phase material is inferred to 108 kN/cm² and 1350 °C, respectively. The resulting pellets show surfaces of two different sized crystallites in the 3–10 µm and 50–150 µm ranges and grains with cheese-like pores of 5–7 µm in the interior. The interior grain size increases with compaction pressure to up to 150–250 µm, while the pore size stays unaffected.

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1. Introduction

M-type hexaferrites AFe_{12}O_{19} (A = Sr, Ba) are materials widely used in industry to manufacture permanent magnets [1–3], due to their strong uniaxial magnetocrystalline anisotropy as well as high chemical and temperature stability. Particularly during the last two decades they were additionally developed as prospective materials for microwave device applications for the frequency range from 1 to 100 GHz [4–9]. Furthermore, hexaferrites were shown to present high potential in many areas like, for example, for high density memory storage applications, magnetic composites and in cancer therapy [10,11].

Barium hexaferrite can be synthesized by a variety of different techniques [22], which give specific (dis)advantages for the respective application, as there are the sol-gel hydrothermal method [12], the auto-combustion method [13], the mechanical activation [14], the mechanical alloying method [15,16], and the ceramic method [16–18]. Additionally, a number of crystal growth techniques have been established like, for example, solid state single crystal growth [19], flux growth [20], and the floating zone technique [21]. Apart from these techniques, the synthesis of submicron ceramic powder materials is a rather difficult task, since the synthesis has to be carried out in a comparably low-temperature region to minimize grain growth, often resulting in multiphase products due to insufficient diffusion between components in chemical reactions [23–26]. Another important characteristic of synthesis from multi-component powders is the necessary high degree of homogeneity.
of the initial component distribution during all process stages to finally obtain high-quality single phase material [27,28].

The magnetic properties of hexaferrite materials substantially depend on the amounts of impurity phases, substituting metal ions and defects within the crystal structure, and the particle size distribution, which all in turn are determined by the preparation method, specifically by the degree of mixing and homogeneous distribution of the precursor materials, compaction pressing conditions and thermal treatment. In this sense, tabletizing via compaction applying an external pressure is an important step in the preparation of ferrite products. Compaction pressing parameters influence many properties of the product: density, strength, hardness, grain size, and pore diameter to name only few. The magnetic permeability, coercive field, ferromagnetic resonance line width, and saturation magnetization depend on the sample density. Important—but not well studied—factors to obtain a material with optimal properties concern the influence of the compaction pressure applied to the barium hexaferrite powder on the magnetic parameters of the resulting material after calcination. One should expect the highest permeability, coercive field and saturation magnetization for samples with the maximum density. The influence of compaction pressure on density, crystal lattice parameters, morphology and magnetic properties has been investigated in this work. Despite the great practical importance, to the best of our knowledge, the influence of the compaction pressure on material properties was hardly studied before [29,30]. Here we study optimal pressure and temperature conditions for pelletizing and calcination of iron oxide/barium carbonate mixtures up to 149 kN/cm² and temperature regime. At the second stage the resulted powder was reground and pressed into tablets with various pressure loads for varying the influence on the microstructure and properties of the finally obtained material. Samples of about 0.3 g mass were used as initial components with batch compositions of 17.08 wt% BaCO₃ and 82.92 wt% Fe₂O₃ (atomic ratio n(Ba): n(Fe) = 1: 12). Both components were mixed and ground in an agate mortar for 1 h. At the first stage the loose powder was calcinated at 1100, 1250, 1300 or 1350 °C for three hours to determine the optimal temperature regime. At the second stage the resulted powder was reground and pressed into tablets with various pressure loads for varying the influence on the microstructure and properties of the finally obtained material. Samples of about 0.3 g mass were pressed into pellets of 5 mm diameter and subsequently calcined in platinum crucibles in a horizontal SIC tube furnace. The sizes of calcined tablets were measured with use of a high-accuracy micrometer (resolution = 0.001 mm). From cylinder diameter and height the sample volume was calculated and the apparent density derived.

The composition of calcined samples was investigated using an energy dispersive X-ray fluorescence spectrometer Oxford INCA X-max 80 attached to a scanning electron microscope Jeol JSM7001F. The chemical composition was calculated as average of ten measurements taken on 1 x 1.5 mm areas of the calcined and reground tablets. X-ray diffraction powder analysis was performed on a powder diffractometer Rigaku Ultima IV in the angular range from 10 to 90° in 2θ with the speed of 2°/min with filtered CuKα radiation. For these measurements the samples were thoroughly powdered and placed on a single-crystalline silicon holder. The phase identification and cell parameters calculation was carried out using the Rigaku PDXL software.

The Curie temperatures were measured using a simultaneous thermal analyzer Netzsch STA 449C Jupiter with differential scanning calorimetry (DSC) method. The samples were placed into a platinum crucible and heated in air at a rate of 2 K/min from 30 to 600 °C. The Curie temperatures were determined as average of the peak maxima of two heating cycles.

Measurements of magnetic properties were performed on a vibrating sample magnetometer VSM LakeShore 7407 at 300 K in external field of 0–15 kG.

3. Results and discussion

3.1. Optimal time-temperature regime

To identify an optimal low reaction temperature coupled with short calcination durations for eventual synthesis of high-density single phase BaFe₁₂O₁₉ material with small grain sizes well ground mixtures of Fe₂O₃ and BaCO₃ in appropriate molar ratios were heated at temperatures of 1100, 1250, 1300, and 1350 °C for 3 h. PXRD allows phase analysis and thus progress of hexaferrite formation. The quantitative phase assessment was obtained using software Crystal Impact Match v1.11. Table 1 summarizes the relative composition of the resulting powders indicating single phase material after 3 h firing only at a minimum temperature of 1350 °C. However, the obtained data allow the identification of an intermediate compound: BaCO₃ reacts quickly with iron oxide to form BaFe₂O₄ first. No residual BaCO₃ or BaO was detected even after calcination at temperatures as low as 1100 °C, despite relatively large initial grain sizes of barium carbonate compared to Fe₂O₃. The eventual formation of BaFe₁₂O₁₉ follows in a sluggish reaction of further Fe₂O₃ with the intermediate BaFe₂O₄. The obtained powder X-ray diffraction patterns are presented in Fig. S1.

The fractions of Fe₂O₃ and the intermediate BaFe₂O₄ decline gradually with rising calcination temperature and completely disappear after 1 h at 1350 °C. However, the application of temperatures as high as 1350 °C already leads to increased grain sizes compared to the initial starting materials or products obtained at lower temperatures (grain size after 1100 °C: <5 μm, 1300 °C: <15 μm, 1350 °C: <30 μm (Figs. S2–S10), while at higher temperatures crystal growth was observed [19]). The composition of samples calcined at 1350 °C from EDX corresponds to expected values for BaFe₁₂O₁₉ within experimental error (average composition: 3.03 at% Ba, 37.65 at% Fe, 59.31 at% O giving an atomic ratio of n(Fe)/n(Ba) = 12.43).

Since shorter firing durations at 1350 °C already may lead to single phase hexaferrite materials, experiments with calcination periods of 15, 30, 60, 120, 150, and 180 min at this temperature were carried out: After 30 min the sample still contains about 10 % BaFe₂O₄ and 5 % Fe₂O₃, after 60 min and above the XRD patterns present single phase BaFe₁₂O₁₉. Thus, for the synthesis of barium hexaferrite microcrystalline powder from Fe₂O₃ and BaCO₃ the optimum conditions are calcination at 1350 °C for 60 min to decrease grain growth.

Fig. 1 presents the powder XRD patterns of barium hexaferrite a simulated pattern according to literature crystal structure data (pattern 1) [31], prepared by single crystal growth from Na₂CO₃ flux (pattern 2) [32] and at 1350 °C for 3 h (pattern 1). The positions of the reflections fully coincide. However, reflections with Miller indices 001 (for example 006 at 22.99° and 008 at 30.82°) show increased relative intensities due to texture, most pronounced for sample 2 obtained by grinding of single crystals with hexagonal platelet shape. The still clearly visible texture of sample
were returned into the furnace and calcined for further 9 h. Table 2 summarizes the apparent densities prior calcination as well as after 1 and 10 h of calcination with the obtained magnetic characteristics for saturation magnetization and coercivity.

The morphology of the surface of the pellets after calcination at 1350 °C for 10 h does not depend on the compaction pressure. All surfaces consist of two types of crystals: densely packed well-faceted hexagonal crystals with sizes in the 3–10 μm range and recrystallized larger crystals of 50–150 μm. Fig. 2 shows two exemplary images of surfaces.

The interior morphology of tablets was investigated on freshly fractured surfaces. With rising pressures the grain sizes of crystals after calcination at 1350 °C for 10 h increases from 70–80 μm to 150–250 μm after application of 108 kN/cm² (Fig. 3). Additionally, the grains show internal pores with sizes of 5–7 μm, which are independent in distribution and size on the applied pressure. These pores arise from secondary coalescence recrystallisation of the fine calcined powder into larger grains. The growing single crystal front propagates through the calcined powder, so that neighboring particles gain the same crystallographic orientation. The compartments between the particles are occluded to form the larger grain and leave pores with sizes primarily depending on the starting powder particle size of 3–30 μm.

Fig. 4 presents the densities of the tablets before and after calcination for 1 and 10 h at 1350 °C depending on the applied compaction pressure. Supposing full occupation of all atomic positions in the crystal structure of BaFe₁₂O₁₉ with an average unit cell volume of 698.3 Å³, the X-ray density calculates to 5.290 g/cm³, which is significantly higher than the obtained apparent densities. The calculated porosity of the densest sample (4.471 g/cm³) equals 15.5%, compared to 20.4% for 4.213 g/cm³ of the pellet with lowest apparent density. During calcination the density of the samples vastly increases. The density of tablets before calcination monotonously rises with the applied pressure, whereas the density after calcination shows a maximum at 108 kN/cm², after which there is a slight decrease. An extension of the calcination duration from 1 to 10 h only for samples pressed at loads lower than 108 kN/cm² increases density, after application of higher loads an increased firing duration has little effect on the final packing density with a tendency even to decrease. The decreasing density of the tablets pressed at 108–149 kN/cm² apparently arises due to crack formation perpendicular to the pressing axis (Fig. 2b). As a result, the optimal compaction pressure corresponds to 100 kN/cm² followed by calcination at 1350 °C for 1 h. Any higher compaction pressures or longer calcination durations are economically unprofitable.

Thermal analysis carried out on samples prepared at various compaction pressures after calcination at 1350 °C for 10 h (Fig. 5) reveals the Curie temperature of 459 °C for all samples. This value is in a good agreement with previously measured data [6]. The magnetic properties of the samples after 10 h calcination are shown in Table 2. The magnet field was oriented perpendicularly to the pressing axis (Fig. 2). Any higher compaction pressures or longer calcination durations are economically unprofitable.

Table 2

<table>
<thead>
<tr>
<th>N</th>
<th>Pressure, kN/cm²</th>
<th>Apparent density, g/cm³</th>
<th>Mₛ, emu/g</th>
<th>Hₑ, Oe</th>
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<td></td>
<td>As pressed</td>
<td>Calced for 1 h</td>
<td>Calced for 10 h</td>
<td></td>
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to the circular tablet pad and parallel to the lateral tablet surface, respectively. It can be noticed that the dependence of resulting $M_s$ on the applied pressure is not monotonic. The reasons lie hidden in the effects of pore volume, grains sizes, self-orientation of these plate-like grains upon increasing size and decreasing aspect ratio, and cracking on the integral magnet moment. The former factors depend on the material morphology and structure. Larger pores as shown in Fig. 3 would reduce $M_s$, while $M_s$ increases with increasing grain sizes obtained after application of higher pressures. However, the main effect reducing the saturation magnetization to values around 51 emu/g appears to be cracking of the pellets during the calcinations procedure. However, a non-monotonic dependence of the coercivity on the compaction pressure can be observed (Fig. 6). The minimum coercivity is obtained for the sample prepared at 121 kN/cm$^2$, which closely correlates with the pressure needed for the maximum density (Fig. 6). In general, calcining after compaction leads to an increased particle growth, which decreases the coercive field until about an applied pressure of 80 kN/cm$^2$. At higher pressures the coercivity appears rather constant within the experimental error.

Fig. 2. Morphology of BaFe$_{12}$O$_{19}$ pellet surfaces of a) after compaction pressure of 67 kN/cm$^2$ and b) 149 kN/cm$^2$ followed by calcination at 1350°C for 10 h.

Fig. 3. Interior morphology of BaFe$_{12}$O$_{19}$ pellets a) after compaction pressure of 50 kN/cm$^2$ and b) 108 kN/cm$^2$ followed by calcination at 1350°C for 10 h.

Fig. 4. BaFe$_{12}$O$_{19}$ tablet density before (black squares) and after calcination at 1350°C (1 h: red circles, 10 h: blue triangles) as function of the applied compaction pressure prior annealing. The calculated X-ray density corresponds to 5.290 g/cm$^3$. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 5. DSC curves of BaFe$_{12}$O$_{19}$ samples pressed under 50, 108 and 134 kN/cm$^2$ after calcination for 10 h at 1330°C.
4. Conclusion

Solid state calcination produces single phase BaFe$_{12}$O$_{19}$ material from mixtures of Fe$_2$O$_3$ and BaCO$_3$ at the optimal conditions of 1 h calcination at 1350 °C. The highest apparent tablet density after calcination was obtained after compaction at a pressure of 108 kN/cm$^2$ and the minimal coercivity detected for 121 kN/cm$^2$. The Curie temperature of 459 °C is rather independent on the compaction pressure, while the coercive field scales with the apparent density. The saturation magnetization depends on pressure nonmonotonically.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.jmmm.2017.11.085.

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[26] C. The highest apparent tablet density after calcination at 1350 °C for 10 h.

Fig. 6. Coercivity of BaFe$_{12}$O$_{19}$ pellets depending on the applied compaction pressure prior firing at 1350 °C for 10 h.