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New results of the crystallization behaviour of hexagonal barium ferrites from a glassy matrix.

5 – Ferroelectrics, ferromagnetics and multi-ferroics

Abstract

Starting from thermoanalytic measurements of amorphous material with a composition of 40 BaO – 33 B_2O_3 – 27 Fe_2O_3 (mole - %) the onset temperatures of four exothermic reaction peaks have been obtained. On the basis of this results the amorphous material was tempered under different conditions (heating rate and tempering time). The resulting reaction products were analyzed by X – ray diffraction, REM, TEM, chemical analyses and by a vibrating sample magnetometer to obtain informations about their chemical composition, their structure and their magnetic properties.

In contrast to former studies [2,3,4] it was found, that first an iron – rich phase forms at temperatures about 520 °C – 560 °C [5] followed by the crystallization of BaB_2O_4.

1 Introduction

Modern applications like high - frequency absorption, perpendicular recording, micro actuators or medical applications for hyperthermia require special properties of magnetic powders like certain aspect ratios, particle sizes or special occupations of the lattice sites. These properties can not be achieved by conventional sintering processes. The crystallization of barium hexaferrite ($BaFe_{12}O_{19}$, BHF) by the “glass crystallization method” [1] offers a large potential to influence these properties.

Besides the variation of the melting and crystallization conditions, the partial substitution of iron oxide (Fe_2O_3) by suitable pairs of metal oxide ions (e.g. CoO / TiO_2, ZnO / RuO_2) shows a high potential for influencing the electromagnetic properties of the ferrite [1].

A new way of controlling this substitution of iron oxide could be created by using high magnetic fields during the crystallization of amorphous flakes. To achieve this goal it is necessary to completely understand how the hexagonal barium ferrites crystallize in a glassy matrix. Further it is important to know possible intermediate products appearing

during the crystallization process. Former investigations of the crystallization of BHF often resulted in contradictory statements. In some works ([2], [3]) the first crystallizing phases are identified as borates (BaB_2O_3, BaB_4O_7) and other authors ([4], [5]) found that at first hexagonal barium ferrite appears.

In this work new results of the crystallization of BHF in glass of the composition 40 BaO – 33 B_2O_3 – 27 Fe_2O_3 (mole - %) are shown. Thermoanalytic methods like differential scanning calorimetry (DSC) and thermo gravimetric analyses (TGA) are used to obtain information about the crystallization process. X – ray powder diffraction measurements (XRD) are performed to analyze the crystalline phases. The morphology and size of the nuclei and crystals are investigated using the transmission electron microscopy (TEM) and scanning electron microscopy (SEM).

Based on this results we plan first tempering experiments with doped amorphous material to check possible influences of high magnetic dc - fields on the substitution of iron ions by other paramagnetic ions and influences on the crystallization process itself.

2 Experimental

The materials used in this work are amorphous flakes of the above mentioned composition, obtained by the rapid quenching process [1]. For further treatment the material is ground to <63 µm and thermoanalytically analysed with a STA 409 PC “Luxx” (Netzsch) using a heating rate of 5 K/min. As a result of this measurements two curves are obtained. From the DSC – curve important temperature - dependent information for the following tempering process (glass transformation temperature and temperatures of exothermic and endothermic reactions) can be obtained. The TGA – curve contains information about possible mass gains or mass losses caused by temperature - dependent oxidation or reduction processes. To find out which phases crystallize at certain peaks of the DSC – curve tempering experiments in a high temperature furnace (ZZ 40-360/13, Gero Hochtemperaturöfen GmbH) are performed. Therefore the sample is heated to the selected (DSC-) onset – temperature with a heating rate of 5 K/min, remained for 10 min and then cooled down to room temperature. After that the sample is ground again (<63 µm) and then analysed by XRD (Siemens AXS “D5000”, wavelength: 1.540598 nm). To investigate appearing ferrite crystals it is necessary to dissolve other phases (surrounding borates) by a weak acid (acetic acid: CH_3COOH). The undissolvable ferrite powders are analysed again by XRD. The estimation of the crystal morphology and size is done with a transmission electron microscope (TEM, Phillips

Tecnai S20). Magnetic measurements are performed with a vibrating sample magnetometer (VSM 7300, Lake Shore). The real chemical composition of the sample material is obtained by chemical analyses (titration with EDTA/ $ZnSO_4$, ICP– OES).

3 Results and discussion

The results of the thermoanalytic measurements are shown in Fig.1. Beside the glass transformation temperature T_G at 490 °C four exothermic peaks with onset temperatures of 524 °C (P01), 560 °C (P02), 606 °C (P03) and 669 °C (P04) are present. The thermo gravimetric curve shows a mass gain of about 0.2 wt-% starting at a temperature of about 200 °C. This mass gain is caused by the oxidation of Fe^{2+} to Fe^{3+} which was also confirmed by chemical analyses.

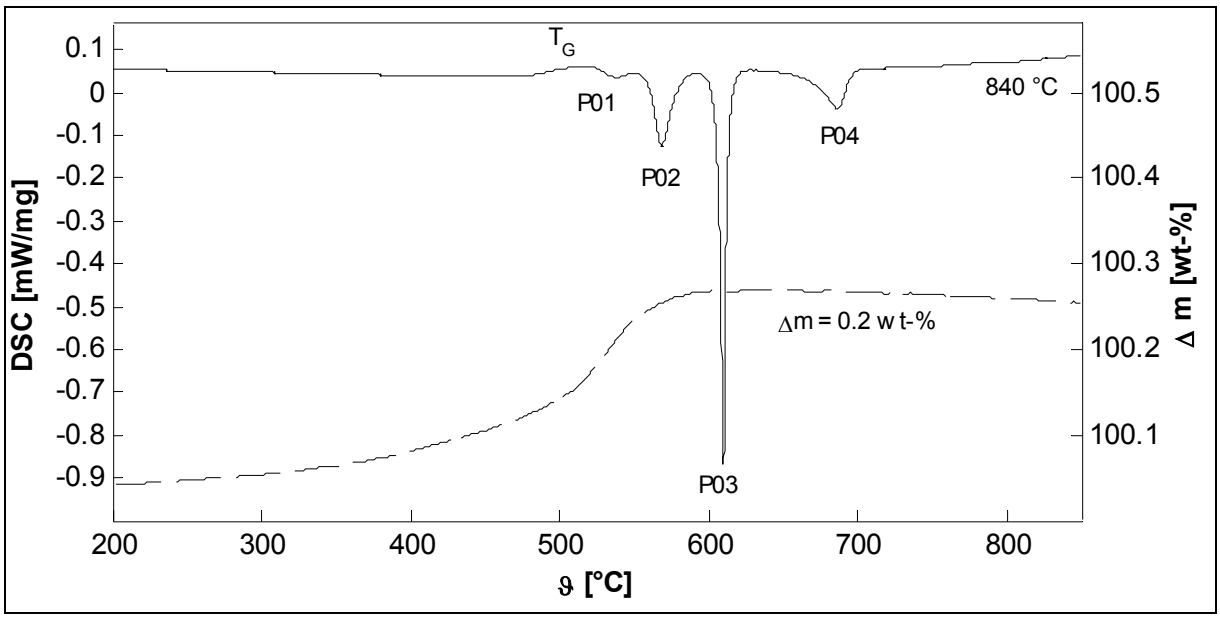

Fig. 1: DSC and TGA curves of the amorphous flakes (5 K/min, m_{sample} = 326,166 mg)

The XRD diagrams of the tempered (undissolved) material are shown in summary in Fig.2. The spectrum of the untreated flakes shows no peaks but halos which reflect the amorphous character of this samples. For the material tempered at 524 °C these halos become more intense. This could be caused by beginning reorganization processes within the material. After tempering at a temperature of 560 °C the intensity of these halos decreases and a small broad peak appears at 2Theta = 62° (Fig. 2 marked area). At a tempering temperature of 606 °C characteristic peaks of BaB_2O_4 and first small peaks of BHF appear and also remain at higher tempering temperatures. At 669 °C further peaks appear. These peaks can also be associated with crystalline $BaFe_{12}O_{19}$.

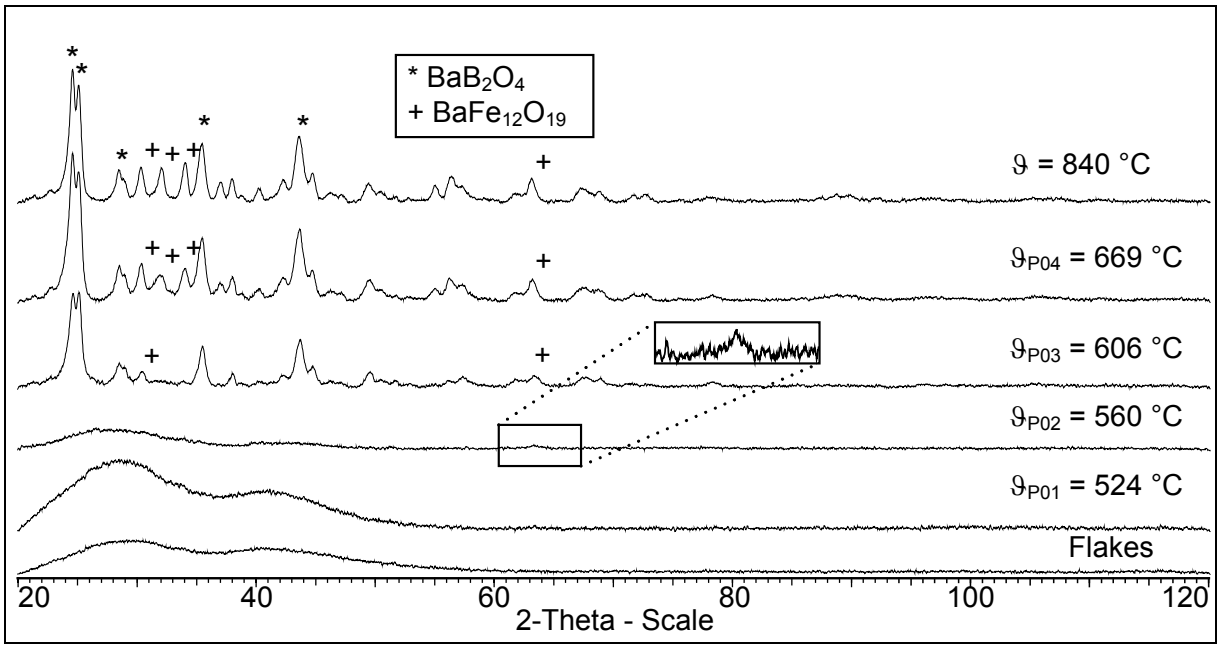

Fig. 2: XRD diagrams of the undissolved sample material tempered at the onsets of the peaks obtained from the DSC – measurement

The amorphous flakes as well as the material tempered at 524 °C don't leave a residue after dissolving in the weak acid. The diffraction diagrams of the material obtained after tempering at ϑ ≥ 560 °C and the dissolving process are shown in Fig. 3. The first crystalline material can be obtained only after dissolving the sample tempered at 560 °C.

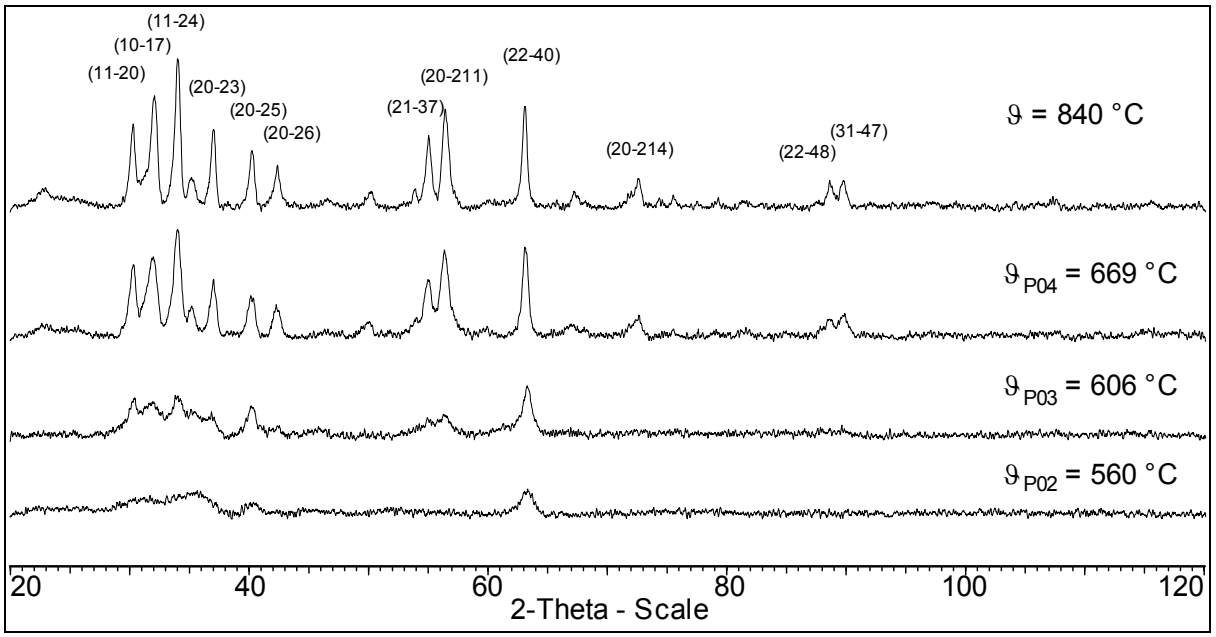

Fig. 3: XRD – diagrams of the residues remaining after dissolving the tempered samples

Due to the very low intensity and strong broadening of the peaks this material can't be clearly identified by XRD. Chemical analyses (ICP) of this material showed a very high iron content (Ba/Fe = 1/19), which could also be verified by wet chemical anlyses

(complex titration). The theoretical ratio Ba/Fe of M-type barium hexaferrite is Ba/Fe = 1/12. After tempering at 606 °C and dissolving the surrounding phases the remaining powder can clearly be identified as M-type barium hexaferrite $BaFe_{12}O_{19}$. With rising tempering temperature the peaks become more intense and more narrow which can be attributed to the increasing perfection of the crystals. This can also be approved by TEM investigations of the tempered and suspended material. At low tempering temperatures the images of the residue show nuclei with a diameter of about 5 nm (see Fig. 4 left).

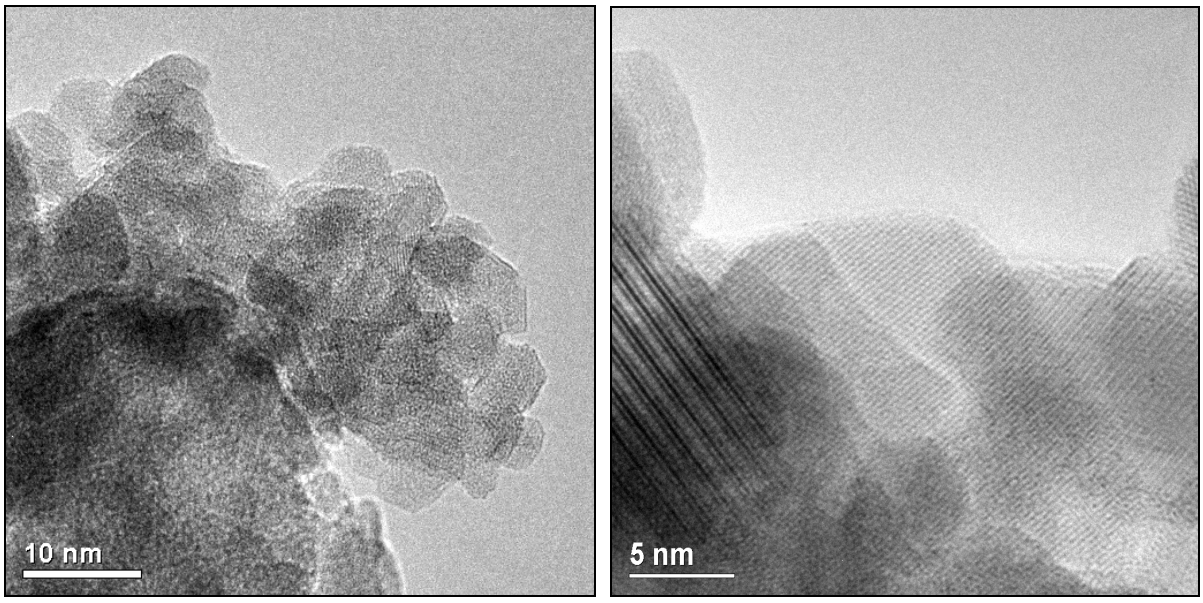

Fig. 4: TEM images of the material tempered at 560 °C (left) and 606 °C (right)

When tempered at a temperature of 606 °C the nuclei grow and become crystals (Fig. 4 right). At 669°C they reach diameters of about 50 nm (Fig. 5 left).

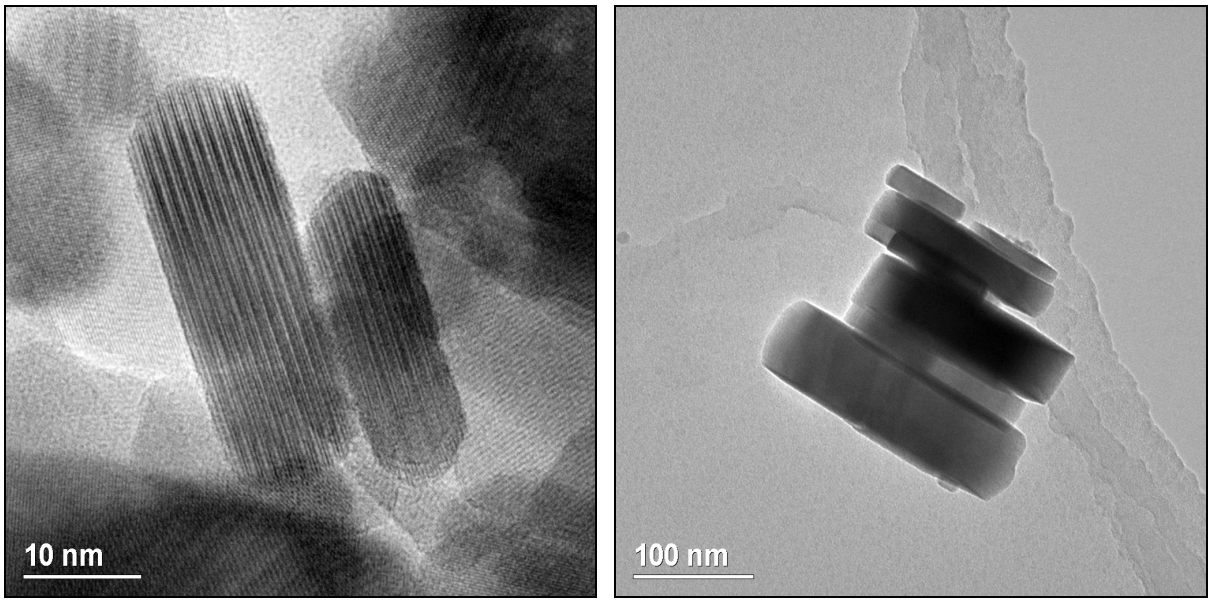

Fig. 5: TEM images of the material tempered at 669 °C (left) and 840 °C (right)

An increase of the tempering temperature to 840 °C results in a further growth of the crystals to diameters of about 200 nm (Fig 5 right) and a morphology transformation from a hexagonal bipyramidal into a hexagonal plate - like form (see also Fig. 6).

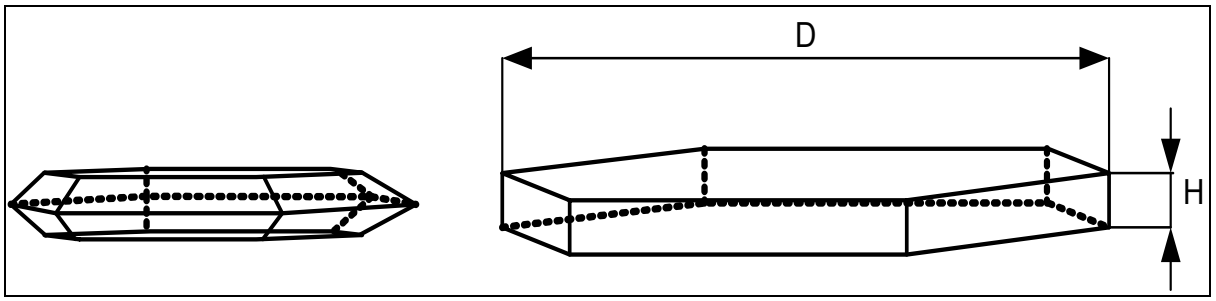

Fig. 6: Schematic drawing of the morphology change from a hexagonal bipyramidal to a hexagonal plate - like form

The measurements performed with a vibrating sample magnetometer show that even tempering at low temperatures (524°C) affects the magnetic properties of the sample material. Fig. 7 shows the curves of the untreated (and undissolved) amorphous flakes (BHF11_2|0a) and of the undissolved material tempered at 524°C (BHF11_2|1c).

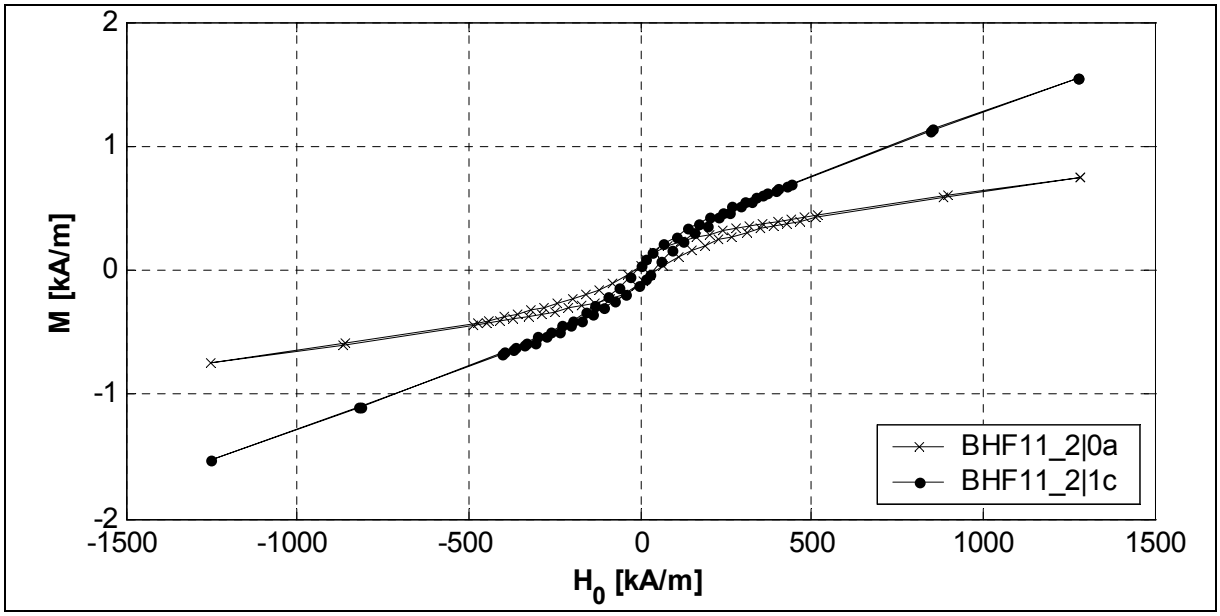

Fig. 7: VSM measurements of the untreated amorphous flakes (BHF11_2|0a) and of the undissolved sample material tempered at 524°C (BHF11_2|1c).

The ferromagnetic behaviour increases leading to an increasing nonlinearity of the curve and rising remanent magnetization with rising tempering temperatures which could be an indication of phase separations or changes within the atomic distribution of the material. This results confirm the XRD measurements of the same materials shown in Fig. 2.

As mentionened above the further increase of the tempering temperatures leads to an increase in particle size and perfection. This as well can be verified by VSM measurements. Fig. 8 shows the measurements of the dissolved material tempered at

560°C (BHF11_2|2f), 606°C (BHF11_2|3b), 669°C (BHF11_2|4d) and 840°C (BHF11_2|5d).

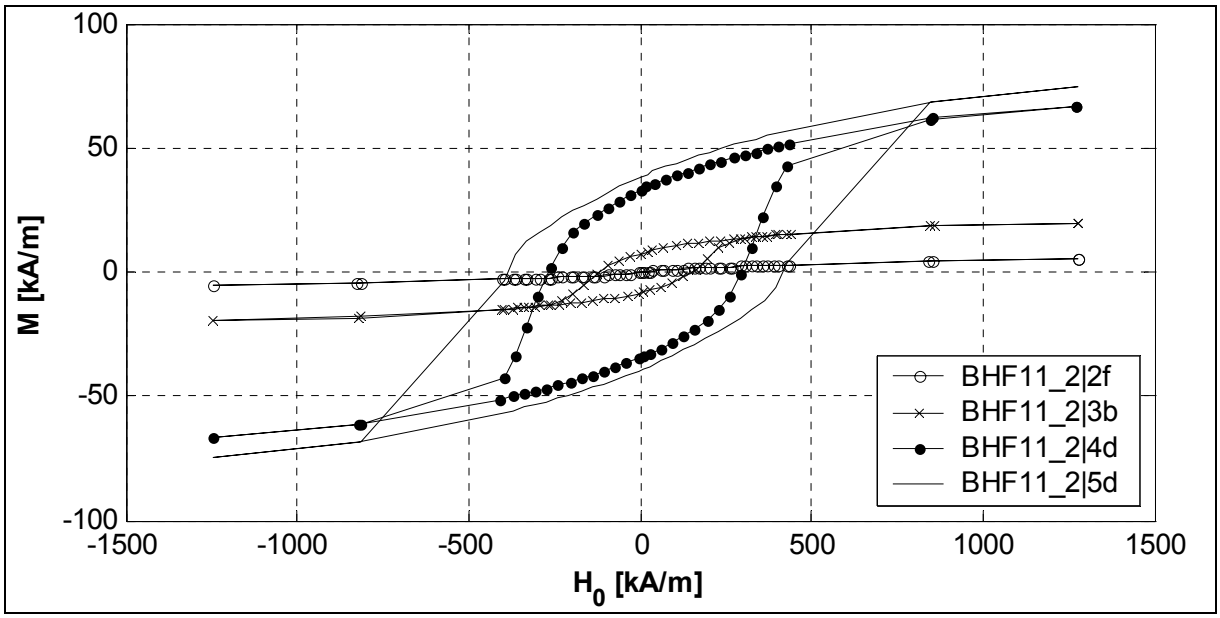

Fig. 8: VSM measurements of the dissolved sample material tempered at 560°C (BHF11_2|2f), 606°C (BHF11_2|3b), 669°C (BHF11_2|4d) and 840°C (BHF11_2|5d).

As expected the increase in size and perfection of the crystals reflects in increasing magnetic properties of the material.

4 Conclusions

The crystallization of undoped BHF - crystals in amorphous flakes of a composition of 40 BaO – 33 B_2O_3 – 27 Fe_2O_3 (mole - %) was analysed. Thermoanalytic measurements showed, beside the glass transformation temperature, four exothermic reactions, which were investigated by XRD and TEM (Tab. 1).

Tab. 1: Tempering temperatures and reactions

Tempering Temperature	occurring reactions
490 °C	• Glass transformation temperature
524 °C	• Oxidation of Fe^{2+} to Fe^{3+}
560 °C	• Precipitation of a crystalline phase not yet clearly identifiable, D ~ 5 nm)
606 °C	• Precipitation of BaB_2O_4, • growth of ferritic particles ($BaFe_{12}O_{19}$,, D ~ 20 nm)
669 °C	• Further growth of $BaFe_{12}O_{19}$ (D ~ 50 nm) crystals within BaB_2O_4 matrix • Crystals of hexagonal bipyramidal morphology
840 °C	• BHF – particle sizes D ~ 100 nm … 200 nm • Morphology of $BaFe_{12}O_{19}$ particles changes to hexagonal plate – like form

No $BaFe_2O_4$ was found during the crystallization. The first appearing crystalline phase at 560 °C is not clearly identifiable by XRD, but analyses showed a high content of iron

(ICP – OES) and ferromagnetic behaviour (VSM).

Based on this results we prepare tempering experiments with doped amorphous flakes to check possible influences of high magnetic dc - fields (> 1 T) on the substitution of iron ions by other paramagnetic ions (Co^{3+}, Ti^{4+}) within the lattice of $BaFe_{12}O_{19}$ and influences on the crystallization process itself. We assume that for such experiments the temperatur range from 490°C up to 560°C is very interesting. Here the mobility of the ions is already high enough and the magnetic interconnections between the paramagnetic ions are sufficiently small.

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