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Investigations of Crystallization Behaviour of Barium Hexaferrite Inside High Magnetic DC Fields

Electromagnetic processing of materials

Abstract

The influence of strong magnetic DC fields on crystallization behaviour of amorphous material in the ternary system BaO-Fe_2O_3-B_2O_3 was investigated by applying the glass crystallization technique [1]. The better understanding of the crystallization process of barium hexaferrite ($BaFe_{12}O_{19}$; BHF) is the scientific goal of this work. Special interest is on the polyvalent paramagnetic cation iron, whose 3d-orbital is not completely occupied with electrons and which possesses four uncompensated spin moments, which produce a permanent magnetic moment.

The starting material are amorphous flakes of a composition of 39,6 BaO - 35,4 B_2O_3 - 25 Fe_2O_3 (mole-%), obtained by a rapid quenching process. To get information about the crystallization process thermoanalytic measurements were made. In subsequent systematic experiments the amorphous flakes were tempered at the four onset temperatures of the DTA-peaks outside and within a magnetic DC field of 5 Tesla. Obtained materials were analysed with XRD.

Experimental

One method to synthesize barium hexaferrite ($BaFe_{12}O_{19}$; BHF) is the glass crystallization technique. This method starts with flakes prepared in the BaO-Fe_2O_3-B_2O_3 ternary system by a two step melting process [2]-[4]. XRD investigations performed on powdered glass flakes showed no indication for the presence of any crystals. Amorphous flakes are the starting material for all further investigations. The flakes are ground to ≤ 63 µm for all further treatments.

The ground flakes were thermoanalytically analysed with a STA 409 EP (NETZSCH) using a heating rate of 5 K/min. Four exothermic reaction peaks could be determined. To test which crystalline phases crystallize at the certain peaks, the ground flakes were tempered at each onset temperature for two hours [5]. To investigate the influence of strong magnetic DC fields on crystallization behaviour the samples were tempered within magnetic DC field of 5 Tesla and without an external magnetic field (only terrestrial magnetic field). These magnetically assisted investigations were performed inside a supra-conducting, cryogen-free magnet (CRYOGENICS) with a warm bore of 300 mm and a constant magnetic flux density of up to 5 Tesla. At 5 Tesla the obtained magnetic flux density is constant within 0,05 Tesla in the experimentally used volume. The high-temperature furnace (XERION) is specially designed for the insertion into the warm bore of the CFM. Heating is done by an DC heater for minimizing unintended interactions between heating currents and magnetic field, and vice versa. With this assemblage a maximum temperature of up to 1500 °C can be obtained. The temperature profile over the area of maximum temperature corresponding to the experimentally used hot spot is very constant, with a maximum variation in temperature of set point ± 2,5 °C. The hot spot maximum and area of maximum, constant magnetic flux density overlap in the centre of the experimentally used region of 6 cm height and 5 cm diameter. Because of the separately computer controlled devices independent and precise control of magnetic field and temperature is possible. A platinum crucible containing four gram of ground flakes was placed into the hot furnace and taken out of the hot furnace after a residence time of two hours.

After tempering the samples were ground again and analysed with X-Ray powder diffraction (SIEMENS D 5000; Göbel mirror, Cu-Kα-radiation) and thermoanalytical measurements.

During the tempering process, crystallization of ferrite crystals and borates is initiated. By a wet chemical treatment with diluted acetic acid the ferrite crystals were separated from the solvable borates (glassy and crystalline). Obtained unsolvable ferrite powders were analysed again with XRD.

Results and Discussion

Figure 1 shows the DTA-curve obtained from the amorphous flakes. Four exothermic reaction peaks could be determined at 534 °C, 570 °C, 612 °C and 708 °C, belonging to the onset temperatures 522 °C, 552 °C, 594 °C and 684 °C. The glass transition temperature at 490 °C is also visible in the curve.

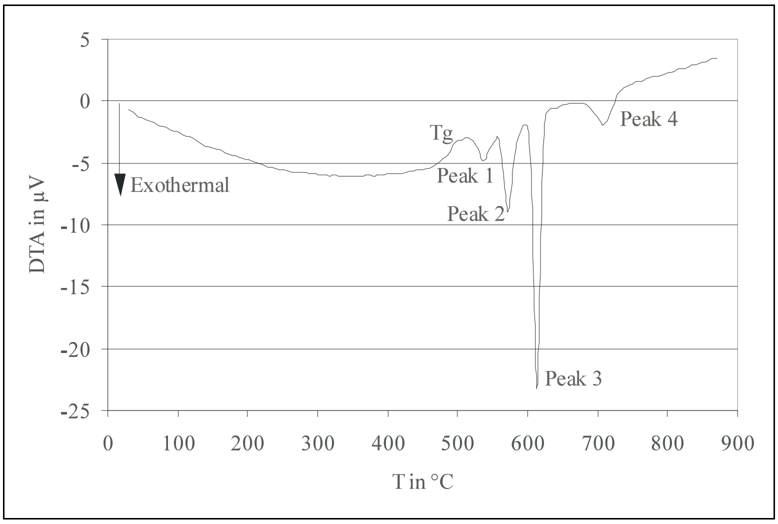

Figure 1: DTA curve of the amorphous, ground flakes (m_{Sample} = 100,5 mg)

The X-ray diffraction pattern of the samples tempered at 522 °C shows a similar curve progression as for the amorphous flakes, no difference between tempering within (5-Tesla-sample) and without (0-Tesla-sample) a magnetic DC field could be determined. Like for the untreated flakes no indication for crystalline phases were found, but two halos, which indicate the amorphous properties and amorphous phase separation.

0-Tesla-samples and 5-Tesla-samples tempered at 594 °C and 684 °C are only different in the intensity of the peaks but not in curve progression. The halos disappeared. With magnetic field and rising tempering temperature the peaks became more intensive and narrow. Consequently the perfection of the crystals increases.

The most significant difference between tempering within and without a magnetic DC field appears if the unsolved samples are tempered at 552 °C. Figure 2 shows the X-Ray diffraction pattern of the untreated amorphous flakes, flakes tempered at 552 °C before the separation and of the powder after the separation, both with and without tempering inside the magnetic field. The pattern of the untreated flakes (curve a) shows only two halos, which as mentioned above indicate the amorphous state. Furthermore the two halos are an indication for two glassy phases, that means phase separation occurs. Then the unsolved tempered samples were compared (curve b and c). The 0-Tesla-sample shows the same two halos, like the untreated sample and some very small peaks, which can be associated with crystalline Borates (BaB_2O_4). A first peak of low intensity coincides with $BaFe_{12}O_{19}$. The same peak was found at the 5-Tesla-sample (curve c) too. Unlike the 0-Tesla-sample halos were unverifiable, the sample hasn't any glassy phase. The intensity of the other peaks is more intensive and can definitely be associated with crystalline Borates. The number of the peaks increases. Surprisingly the DC magnetic field influences more the growth of BaB_2O_4 as of $BaFe_{12}O_{19}$. After separation of the Borates the curve progression between the 0-Tesla-sample (curve d) and the 5-Tesla-sample (curve e) is quite similar. The peaks of the Borates disappear, because they were solved in acetic acid. Three peaks can definitely associated with $BaFe_{12}O_{19}$. The big halo signalises a great amount of strongly disordered, glassy like ferrites.

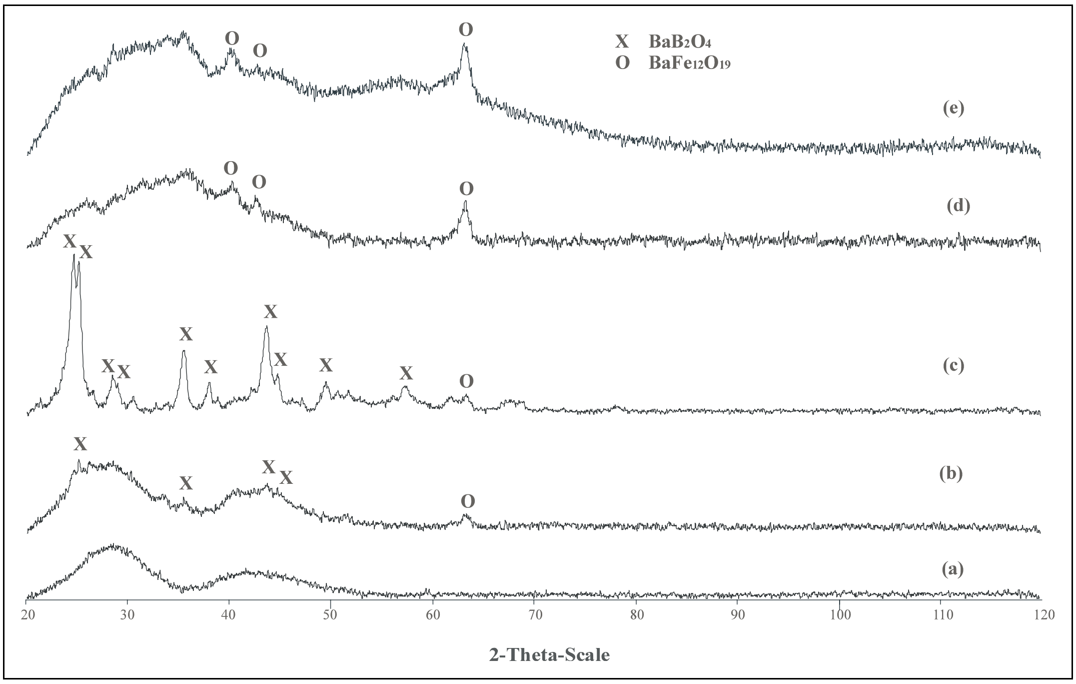

Figure 2: X-Ray powder diffraction pattern

(a) untreated amorphous flakes
(b) at 552 °C tempered Flakes without magnetic field
(c) at 552 °C tempered Flakes with magnetic field (5 Tesla)
(d) at 552 °C tempered Flakes without magnetic field after separation
(e) at 552 °C tempered Flakes with magnetic (5 Tesla) after separation

Conclusion

We investigated the influence of a strong magnetic DC field on the crystallisation process of amorphous flakes of the composition of 39,6 BaO – 35,4 B_2O_3 – 25 Fe_2O_3 (mole-%). By thermoanalytic measurements the maximum temperatures of four exothermic reaction peaks could be determined at 534 °C, 570 °C, 612 °C and 708 °C, belonging to the onset temperatures 522 °C, 552 °C, 594 °C and 684 °C. In systematic experiments the amorphous flakes were tempered at the four onset temperatures outside and within magnetic DC field (5 Tesla). It turns out that the strongest influence of the magnetic field occurs at 552 °C. Unlike the material tempered without a magnetic field, the material tempered within a magnetic field of 5 Tesla shows no glassy phase. The intensity of the X-ray diffraction peaks is more intensive and can definitely associated with crystalline Borates. Differently as expected not the ferric but the borate phases are influenced during crystallization at 552 °C by a magnetic field. This may be a seeming correlation only. Verification of the results and further investigations are the topic of next current works.

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