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THE INFLUENCE OF NANOMILLING ON THE FORMATION OF Ba-HEXAFERRITE

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Abstract. The formation of W-type $Ba(Me)_2Fe_{16}O_{27}$ (Me=Zn, Ni) hexaferrites were studied by synthetizing them, using Fe_2O_3, ZnO, $NiCO_3$ and $BaCO_3$ as starting materials. The synthesis was made in numerous steps. At first some of the starting materials were premilled by high-energy milling (HEM) (Fritsch Pulverisette 4) in different combinations to promote the formation of solid solutions involving the substitution of one divalent cation by another, or by a combination of divalent cations. In the next step presintering of the materials was carried out. After that the material was again milled by HEM using different milling parameters then compacted and sintered. TG-DTA examinations of the outgoing materials and variously prepared milled products were made to reveal the differences in the solid-state reactions, and XRD, SEM, TEM measurements, in order to observe the changes in the crystalline structure, morphology and composition. By the applied procedures good quality W-type Ba-hexaferrite could be observed.

1. INTRODUCTION

Recently there is a considerably interest in the study of different types of hexagonal ferrites, due to their applications in new emerging technologies: at magnetic, electronic and microwave fields. To understand and to improve the technological processes a strict controll of the microstructures (homogeneity, particle size, shape, crystal structure, *etc.*) which governs the intrinsic magnetic behaviour is inevitable [1].

High energy ball milling (HEBM) [2,3] is one of the suitable processing techniques for synthesis of nanocrystalline materials [4] in this manner also for the preparation of nanocrystalline ferrite powders exhibiting new and unusual properties [5]. The mechanical treatment with high energy can change the termodynamic potentials of the reagents and diminish the temperatures of the chemical reactions.

So far the phase transformation processes of Ni and Zn containing W type Ba-hexaferrites produced by differently governed ball milling have not been studied by TG-DTA, XRD, TEM, SEM and other investigation methods.

The aim of our work and microstructural analysis is to clear up and improve the technological steps of this type of W-type Ba-hexaferrite production.

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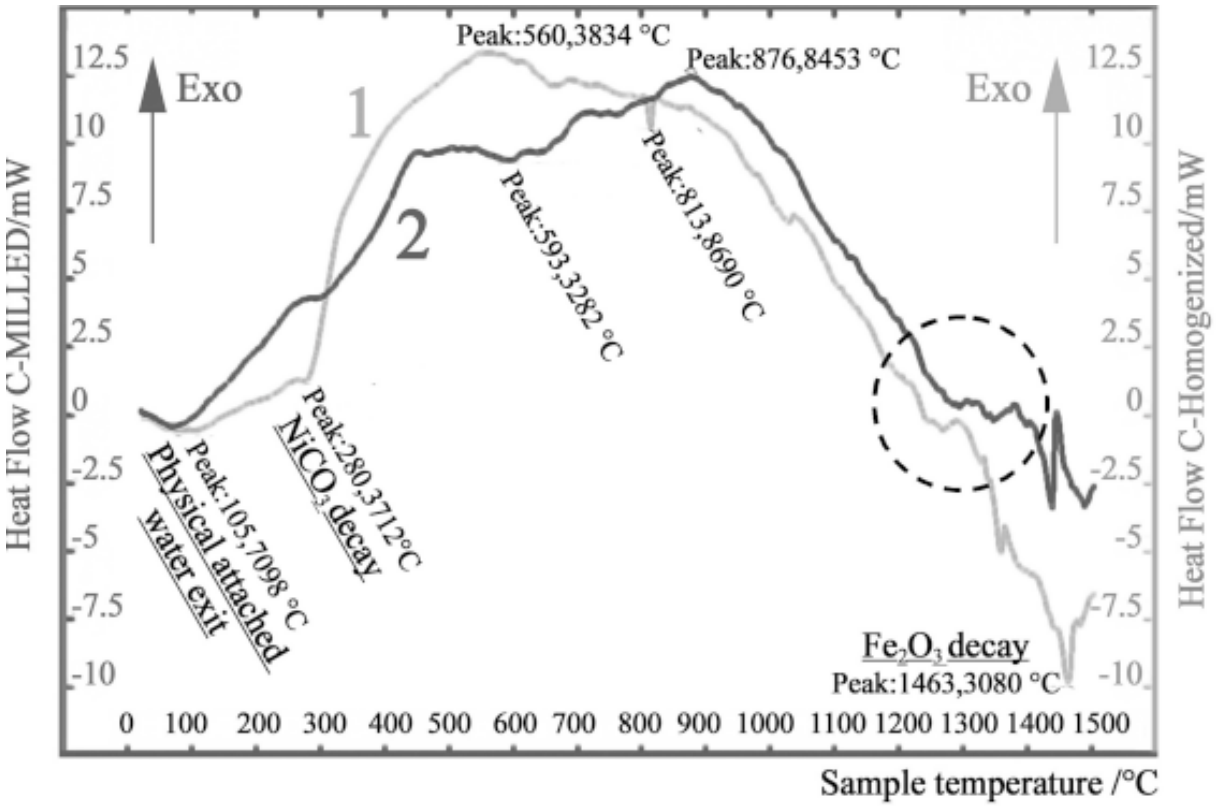

Fig. 1. Comparison of the DTA curves of the homogenized *stoichiometric* mixture of the outgoing materials (**1**) and mechanical milled powders (**2**) (PCMD=360 W, 8h) At the black circle it may be assumed that the formation of ferrite is starting.

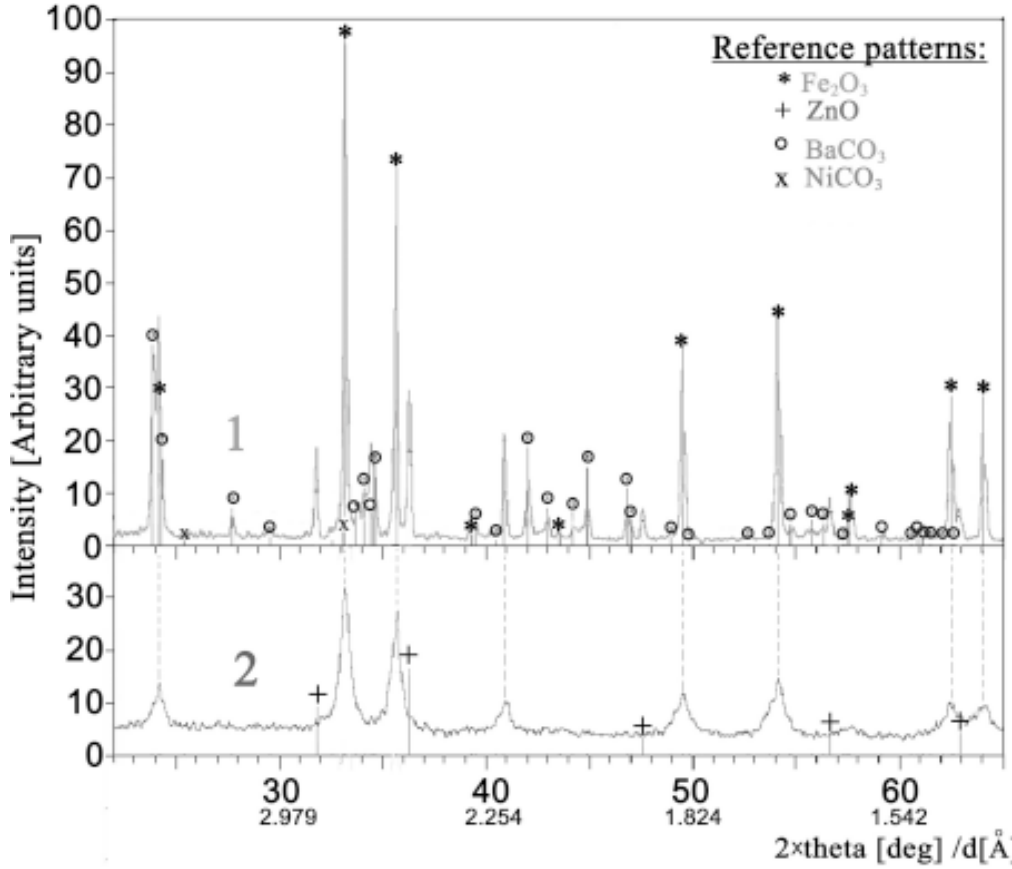

Fig. 2. X-ray diffraction pattern of the homogenized stoichiometric mixture of the outgoing materials (**1**) and mechanical milled powders (**2**).

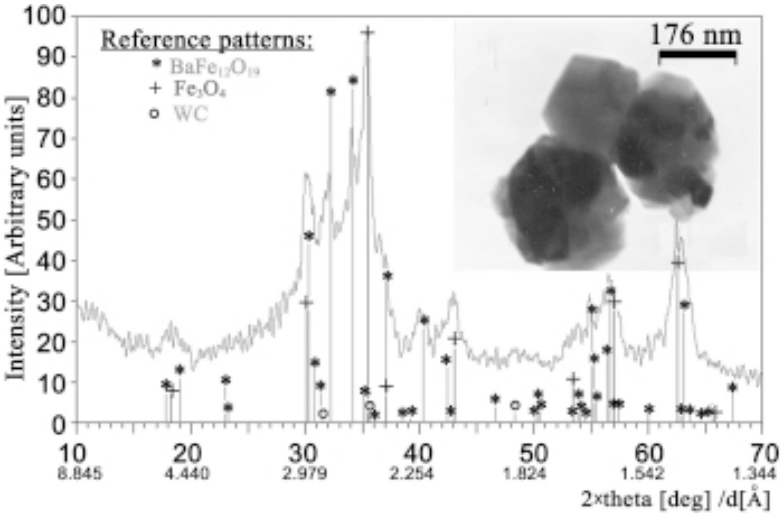

Fig. 3. X-ray diffraction pattern and TEM micrograph of high-energy milled (8h/370W) presintered sample (crystallite sizes of M-type Ba-ferrite ~ 20 nm).

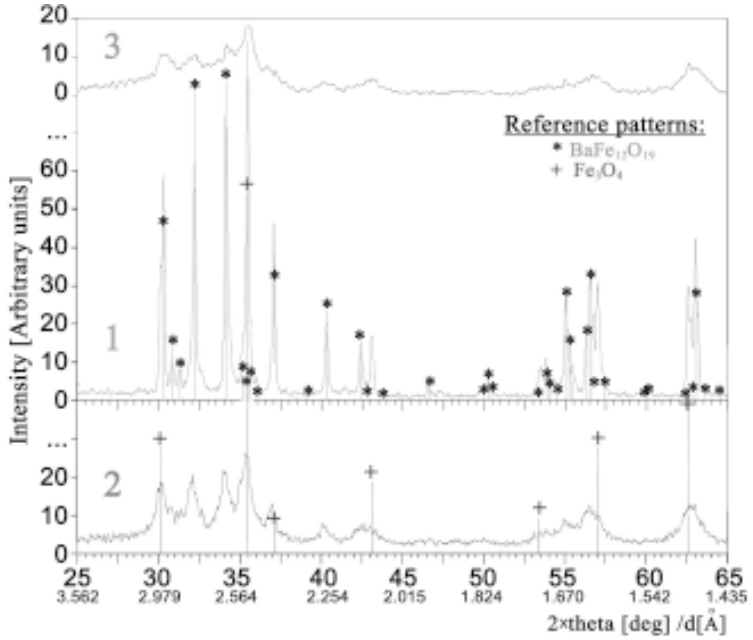

Fig. 4. X-ray diffraction pattern of the conventionally produced presintered sample (1) and after 4 (2) and 8 (3) hours high-energy milling (370 W).

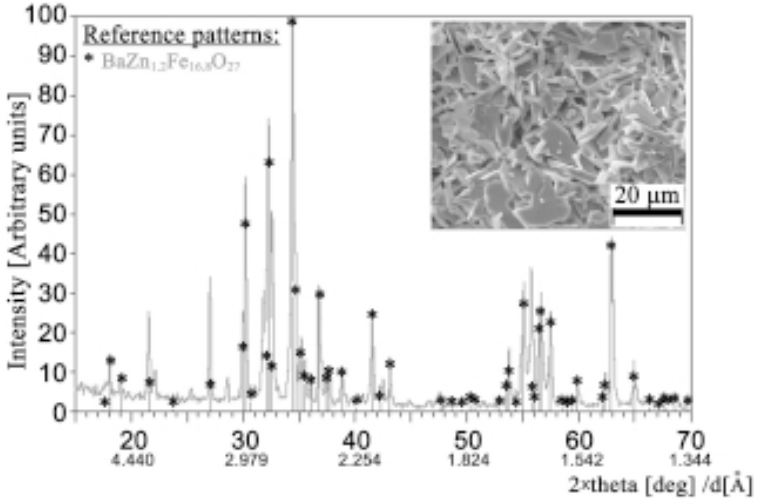

Fig. 5. X-ray diffraction pattern and SEM micrograph of *high-energy milled* W-type Ba-hexaferrite sintered sample.

2. EXPERIMENTAL

The synthesis of high energy W-type $Ba(Me)_2Fe_{16}O_{27}$ (Me = Zn, Ni) hexaferrite formation was carried out in two parts. In the first part HEM of the outgoing materials and a presintering heat treatment (~ 1100 °C) was made by which M-type Ba-hexaferrite was produced. In the second part the M-type Ba-hexaferrite was high energy ball milled, compacted and sintered at a higher temperature as before (~ 1300 °C) to produce the phase transformation:

M-type Ba-hexaferrite $\rightarrow$ W-type Ba-hexaferrite

The mechanochemical synthesis of W type Ba-hexaferrite carried out by low energy millings and heat treatments was compared with the syntheses made by different high energy milling routes and heat treatments.

In course of the experiments a FRITSCH Pulverisette 4 planetary mill was used either with stainless steel or hard metal vials and steel balls and 1:5 ball to powder weight ratio by using different milling parameters. (The milling time: 4 and 8 hours, and PCMD=370 W, AVMD=400 rpm, RR= -2.5, PCMD = Power Consumption of the Main Disk, AVMD=Angular velocity of main disk, RR=Relativ Ratio)

The outgoing materials used in this study were MCO_3 (Reanal) with M = Ba, Ni and ZnO (Reanal) and Fe_2O_3 (Bayferrox) mixed together. The stoichiometric composition of the product should be $Ba(Ni_{0.5}Zn_{0.5})_2Fe_{16}O_{27}$.

All powder handling, milling and subsequent pressing and heat treatments were performed in air.

Characterization of the atomic structure, morphological features, thermal behaviour, magnetic properties were carried out. Crystal structure of the powders was investigated by X-ray Powder Diffraction technique (Philips PW 105, Cu K_α 40kV, 35 mA, Scherrer method). Morphological features of the particles, agglomerates and compacted samples were studied by SEM (Hitachi S-570, Röntec EDS) and TEM (Jeol 200A). Thermal behaviour of the powders was observed by thermal gravimetry (TG) and differential thermal analysis (DTA) (Setaram Setsys 16/18) in flowing synthetic air atmosphere (80%N_2, 20% O_2), in the temperature range of 20-1500 °C, with a heating rate of 10 K/min, in 100 µl Al_2O_3 crucibles.

3. RESULTS AND CONCLUSIONS

1. Regarding the first part of the synthesis:

- all high energy milled samples have shown another type DTA curve as the homogenized (mixed with low energy) stoichometric mixture,
- by HEM from all outgoing components and also from the presintered M-type hexaferrite material nanosized crystallites could be achieved.

It can be observed that the homogenized samples are showing an endothermic peak and all high-energy milled samples (samples of different milling routes) have an exothermic peak (around 800 °C) before reaching the presintering temperature (above 1000 °C). The characteristic DTA lines of the homogenized oxide mixtures and the differently milled variants can be seen in Fig. 1. The crystallite sizes of the outgoing materials (Fig. 2) and also those of the presintered M-type hexaferrite powders (Fig. 3) produced by HEM became nanosized (size is depending on the milling conditions) as it is showing by XRD and TEM, these sizes are much smaller than those produced in the workshop by conventional low energy milling (Fig. 4).

2. Concerning the second part of the process:

- by HEM and sintering the earlier presintered and again high energy milled and compacted M-type hexaferrites transformed to good quality W-type hexaferrites (Fig. 5).
- comparing after sintering the samples produced in the workshop by conventional low energy milling and greenbody forming and those samples produced by HEM both are showing the same W-type Ba-hexaferrite structure (XRD). The fracture of the sintered HEM material is showing plate like grains (SEM) (Fig. 5).

It was shown that high energy ball milling can be used to enhance the synthesis of W type Ba-hexaferrite due to the much smaller crystallite sizes and much larger surfaces of contact produced between the components and because of their activation.

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