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High coercive barium hexaferrite powders by partial Ba^{2+}- and Fe^{3+}-substitution for magnetic sensor applications

5 – Ferroelectrics, ferromagnetics and multi-ferroics

Abstract

The synthesis of the modified barium hexaferrite (BHF) powders and the adjustment of the magnetic properties for sensoric applications are realized by the glass crystallization technique in the system BaO-Fe_2O_3-B_2O_3. Two ways for modification of the BHF-powders were used. The first possibility is the partial substitution of the oxides in the basic melt by other oxides (e.g. Fe_2O_3 by Al_2O_3 and BaO by SrO). The second way is the variation of the process conditions. The obtained modified powders were analyzed for their crystallographic structure, chemical composition, particle morphology and magnetic properties. The nanoscaled powders with modified magnetic properties open a wide application field. One application is, to use it in flexible powder filled cellulose fiber sensor for position detection in the micro processing technology and micro measurement technology.

1 Introduction

Hexagonal ferrites have a lot of potential applications, because their magnetic properties are good adjustable. This applications range from ceramic permanent magnetic material, magnetic recording media, hyperthermia in medicine to chemical and electro magnetic absorbing materials [1].

In this work we report results of the sythesis of submicron down to nanoscaled modified barium hexaferrite powders for sensor applications. Thereby the main aim was to increase the hard magnetic properties (saturation magnetization, coercivity) of the powders. For the synthesis of the powders the glass crystallization technique in the system BaO-B_2O_3-Fe_2O_3 with the chosen basis composition 40 mol-% BaO, 33 mol-% B_2O_3 and 27 mol-% Fe_2O_3 was used.

The investigations are divided into two parts. The first part is to improve the magnetic

properties by changing the process conditions for melting and crystallization of the powders. The second way of modification is the substitution of Ba^{2+} and Fe^{3+} ions by other ions (e.g. Al^{3+}, La^{3+}, Sr^{2+}).

In [2] investigations of strontium hexaferrites show, that the coercivity increases by substituting Sr^{2+} by La^{3+} and Fe^{3+} by Co^{2+} without changing the remanent magnetization. The strontium hexaferrites were produced by a ceramic method. Other investigations were made to substitute the Fe^{3+} by Al^{3+} by a wet chemical method [3]. Thereby the coercivity increases, but the saturation magnetization decreases.

In our work the glass crystallization technique was used to modify the powders and to increase the magnetic properties. The achieved powders were analyzed for their chemical, crystallografic and magnetic properties.

2 Experimental

The samples were prepared using the glass crystallization technique. For the synthesis the composition of 40 mol-% BaO, 33 mol-% B_2O_3 and 27 mol-% Fe_2O_3 was used. The glass crystallization technique is subdivided into several steps. Fig. 1 shows the schematic drawing of the glass crystallization technique.

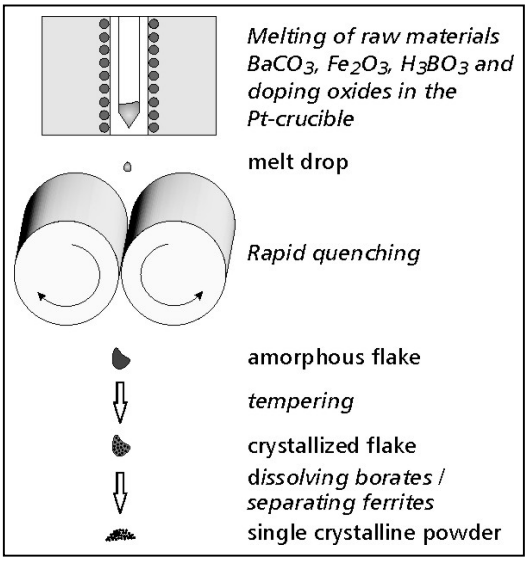

Fig. 1: Schematic drawing of the powder preparation by glass crystallization technique.

At first the raw materials ($BaCO_3$ for BaO, H_3BO_3 for B_2O_3, and Fe_2O_3) were melted inside a platinum crucible for 2 hours at 1350 °C. Then the melt was quenched on a water cooled twin roller to achieve amorphous (glassy) flakes. These amorphous flakes will be tempered in a laboratory furnace at temperatures higher than the glass transformation temperature but below the former melting temperature. During this temperature treatment barium hexaferrite crystals and barium borates grow inside the flakes. These multi phase flakes were filled into a vessel with diluted acetic acid (20 %) for 30 minutes. While solving the barium borates, the barium hexaferrite crystals stay unsolved. Finally the ferrite crystals were separated from the solution by a centrifuge, washed and dryed.

For the modification of the powders the $BaCO_3$ in the raw materials was substituted by $SrCO_3$ or La_2O_3 and the Fe_2O_3 was substituted by Al_2O_3 or CoO (in the case of La^{3+}/Co^{2+}

substitution for the compensation of valencies inside the powder). Tab. 1 shows the compositions and the conditions of the melts for the powder preparation.

Tab. 1: Compositions (in mol-%) and process conditions of the melts for the powder preparation

Melt	BaO	SrO	B_2O_3	Fe_2O_3	Al_2O_3	CoO	La_2O_3	Melt Conditions
BHF (undoped)	40	-	33	27	-	-	-	2 h at 1350°C or 1400°C
Sr1	35,5	4,5	33	27	-	-	-	2h at 1350 °C
Sr2	39	1	33	27				
Sr3	-	40	33	27	-	-	-	
Alu1	40	-	33	23,4	3,6	-	-	
La1	40	-	33	23,4	3,6	-	-	
LaCo x=0,2	39,1	-	33	26,55	-	0,9	0,45	
LaCo x=0,4	38,2	-	33	26,1	-	1,8	0,9	

For the characterization of the amorphous flakes and the crystalline phases a X-ray diffractometer with CoKα-radiation (λ = 1,78897 Å, Bruker AXS D8 advance) was used. The crystallization behavior of the amorphous flakes was analyzed by DSC measurements (STA 409 PC/4/H luxx, Netzsch). The chemical composition of the samples was investigated after wet chemical decomposition with 4 M HCl by ICP-OES (Vista-MPXTM, Varian). Further the morphology and particle size distribution were analyzed by scanning electron microscopy (ESEM XL30, FEI). Thereby the diagonal and the thickness of the hexagonal shaped crystals were measured. For every dimension a minimum of 20 values was estimated to get good average values for the crystals. Fig. 2 shows a schematic drawing for the dimensions a* (diagonal) and d (thickness).

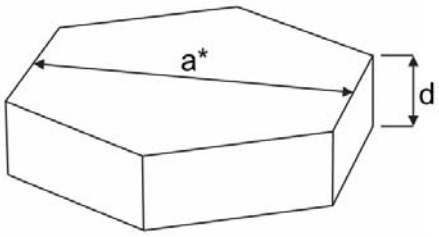

Fig. 2: Schematic drawing of one barium hexaferrite crystal with the measured dimensions a* and d

For the investigation of the magnetic properties the hysteresis loops of the samples were measured in a vibration sample magnetometer (VSM 7312, Lake Shore). From these hysteresis loops the saturation magnetization M_S and coercivity $_JH_C$ were determined.

3 Results

The investigation of the different doped flakes for their structure and crystallization behavior was the first step before the crystallization. The XRD-analysis showed that all of the used flakes were amorphous. These amorphous flakes were analysed by DSC-analysis. Thereby only small changes in the DSC-signals of the different dopings are achieved. The biggest differences were found for the flakes of the melt with the highest strontium content (Sr3). Fig. 3 shows the DSC-signals of two Sr containing flake samples compared to one of an undoped flake sample.

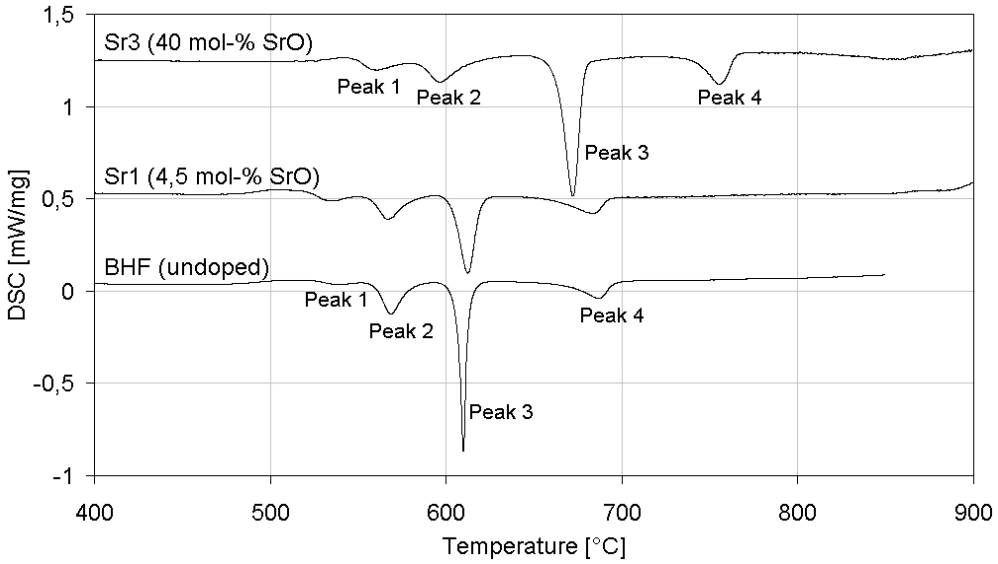

Fig. 3: DSC-signals of Sr containing flake samples compared to one of an undoped flake sample.

The signals show, that the peaks of the samples BHF and Sr1 have almost the same temperature positions, but the intensities and the widths are varying. The third peak (nearly a maximum temperature of 620 °C for Sr1 and BHF) associates with the crystallization of barium hexaferrite [4]. The systematic order of the peaks of sample Sr3 is the same as for the other samples, but the peaks are moved to higher temperatures. This shows, that the strontium hexaferrite has a comparable crystallization behavior to the barium hexaferrite in glass flakes with the same content of barium or strontium. Peak 3 was moved to approximately 670 °C. At this peak the $SrFe_{12}O_{19}$ was detected for the first time.

The prepared powders were analysed by XRD for their crystallographic structure. Thereby all powders (with the different dopings) show only the barium (or strontium) hexaferrite structure. As expected the powder sample with the highest strontium content

(Sr3a) shows only strontium hexaferrite peaks (see Fig. 4).

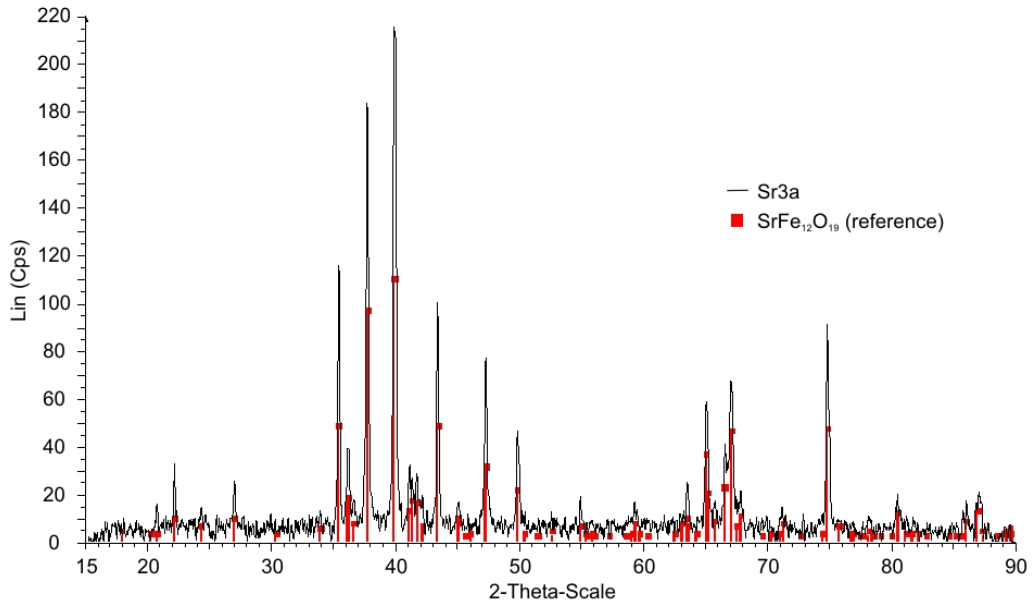

Fig. 4: XRD-diagram of strontium hexaferrite powder (Sr3a) prepared by the glass crystallization technique

Tab. 2 shows the magnetic properties of undoped powder samples made by different conditions but with the same heating rate (infinite, the sample was positioned into the heated furnace) for tempering.

Tab. 2: Magnetic properties and process conditions of undoped BHF-samples with infinite heating rate for crystallization

Sample	Melt-temperature	Crystallization		$_JH_C$	M_S
		Temperature	Time		
	°C	°C	h	kA/m	kA/m
BHF2g	1350	800	2	325,3	76,7
BHF6a	1350	820	2	335,3	118
BHF6c	1350	840	2	362,6	137,6
BHF13b	1400	840	2	362,9	154,4
BHF12b	1350	840	24	381,6	161,4

As observed already earlier by Knauf [5], one result of this magnetic measurements is, that the magnetic properties increase with increasing crystallization temperature and tempering time.

Fig. 5 shows the dependencies of the coercivity and the saturation magnetization by increasing the temperature.

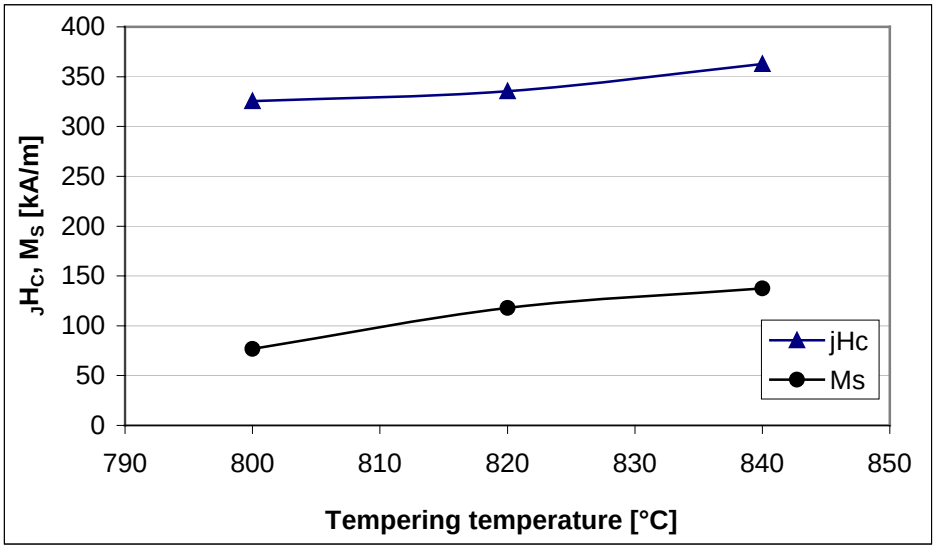

Fig. 5: Dependencies of coercivity and saturation magnetization of undoped barium hexaferrite powders by variation of the tempering temperature with constant tempering time and infinite heating rate (samples were positioned into the heated furnace).

The influence of the crystallization time was tested with one sample, and the magnetic properties increase by longer heat treatment (24 h). A higher melting temperature causes also a higher saturation magnetization.

Further the influence of different doping ions (Al^{3+}, La^{3+}, Co^{2+}, Sr^{2+}) on the magnetic properties was investigated. The magnetic properties and the crystallization conditions of some doped powders are shown in Tab. 3.

Tab. 3: Magnetic properties and crystallization conditions of doped powders with the same melting conditions (2 h at 1350 °C).

Sample	Doping oxides	Doping concentration, melt	Crystallization			$_JH_C$	M_S
			Heating rate	Temperature	Time		
		Mol-%	K/min	°C	h	kA/m	kA/m
Alu1a	**Al_2O_3**	3,6	>>[1]	840	2	374,5	76,5
Alu1b	**Al_2O_3**	3,6		840	24	424,7	57,2
LaCo8	**La_2O_3/CoO**	0,45 / 0,9		800	2	238,3	116,5
LaCo2	**La_2O_3/CoO**	0,9 / 1,8		800	2	235,9	103,9
La1a	**La_2O_3**	3,6		840	2	343,1	94,5
Sr2b	**SrO**	1		840	2	365,5	143,0
Sr1b	**SrO**	4,5		840	2	349,1	118,1
Sr3a	**SrO**	40	5	840	2	432,5	108,9
BHF6c	**Undoped**	0	>>	840	2	362,6	137,6

[1] infinite heating rate: samples were positoned into the heated furnace

The magnetic properties show, that only a few samples, for example Sr2b and Sr3a, are suitable for usage as hard magnetic sensor materials. But powders with magnetic properties in this range can also get achieved by producing undoped barium hexaferrite powders. The expected increased values of La^{3+}/Co^{2+} doped powders were not achieved. One reason of this behavior could be the incomplete substitution of the doping ions inside the lattice of the powders. According to this supposition some of the powders were analysed by ICP-OES after a wet chemical preparation. The results of the ICP-analysis are shown in Tab. 4.

Tab. 4: Comparison between theoretical and analytical (ICP) values of the doping ions of different powder samples and Co^{2+}/La^{3+}-doped flakes

Sample		Concentration [wt-%]					
		Element	theoretical	ICP-Analysis	Element	theoretical	ICP-Analysis
LaCo8	***Flakes***	*Co*	*0,42*	*0,45*	*La*	*0,98*	*0,9*
	Powder	Co	1,06	0,9	La	2,5	0,69
LaCo2	***Flakes***	*Co*	*0,83*	*0,88*	*La*	*1,96*	*1,85*
	Powder	Co	2,12	1,91	La	4,99	0,64
Sr1b	**Powder**	Sr	8,25	0,43			
Sr2b	**Powder**	Sr	1,77	0,17			
Alu1a	**Powder**	Al	4,05	2,64			

The comparison between the values from ICP and the theory show, that the ICP-values for all flakes are approximately near to the theory. But in the powders the content of Co is only 90 percent of the theory, and the content of La is only 0,64 wt-% instead of 2,5 wt-% or 0,69 wt-% instead of 4,99 wt-%. This shows, that great parts of the doping ions, especially lanthanum, do not go inside the ferrite phase during the crystallization. These parts crystallize inside the borate phases and are removed by dissolving the borate phases.

The XRD-diagrams show for the La/Co-doped samples nearly the same peaks as the undoped barium hexaferrite, which is also a sign for the loss of doping ions. With this loss of La inside the powder we can also describe the poor magnetic properties of the La/Co-doped powders.

Among the used tempering conditions maybe the value of approximately 0,7 wt-% La inside the powder is the maximum concentration for La in the powders. In order to achieve higher doping rates, it is necessary to change the tempering atmosphere. With a

reducing atmosphere, it is possible to adjust the valencies of iron and doping ions. Further the Sr- and Al-doped powders show also reduced contents of doping ions inside the powders. This is also a sign, that big parts of the dopands are crystallizing inside the borate phase and so the magnetic properties did not increase in comparison to the sample BHF6c.

The crystal morphology and crystal size were investigated by SEM-measurements. Fig. 6 shows two examples of the synthesized powders.

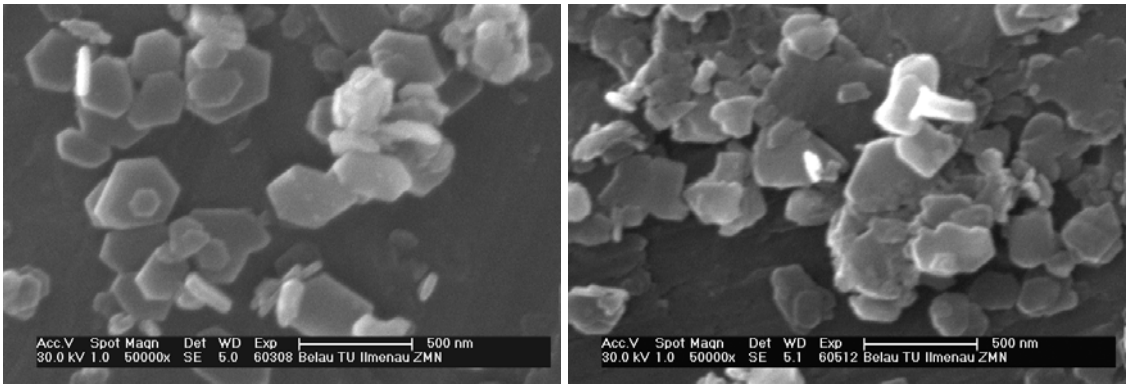

Fig. 6: SEM-pictures of BHF6a (left), Sr3a (right)

The pictures show, that the BHF6a powder has a nearly exact, hexagonal shape. But the sample Sr3a has only a few exactly shaped particles, and the most of the particles have irregular shaped edges. Reasons for this behavior could be the insufficient crystallization conditions (temperature, time) or the diminished solubility of the strontium borate phases in acetic acid. Other doped samples (Al- and LaCo-doped powders) show also nearly exact, hexagonal shapes. The average values for the dimensions of the sythesized powders range from 250 to 350 nm for the diagonal a* and from 57 to 140 nm for the thickness d (see Tab. 5).

Tab. 5: Diagonal a* and thickness d of some powders made by different process parameters

Sample	Crystallization			a* [nm]		d [nm]	
	Heating rate [K/min]	Temperature [°C]	Time [h]	Average value	Standard deviation	Average value	Standard deviation
BHF6a	>>	820	2	261,6	99,5	57,1	30,9
BHF12b	>>	840	24	358,8	138,2	140,3	37,6
Alu1b	>>	840	24	350,7	77,9	119,6	31,5
LaCo2	>>	800	2	325,5	125,6	77,7	33,6
Sr3a	5	840	2	270,8	87,2	62,5	22,2

The standard deviations of the analyzed powders are between 87 and 138 nm for a* and 22 – 38 nm for d. They characterize the wide of the particle distribution.
The wide of the distributions is mainly influenced by the tempering conditions and the doping ion and amount. For the production of smaller particles the time or temperature for crystallization should be decreased. Another way to achieve smaller particles is to use a slower heating rate (e.g. 5 K/min) for the crystallization. Thereby the number of nuclei increases and finally more smaller particles will be achieved than by the usage of infinite heating rate.

4 Applications

For the production of sensor materials the barium hexaferrite powder was filled into diluted cellulose solution, and flexible fibers or fleeces were produced by the Lyocell-process [6].

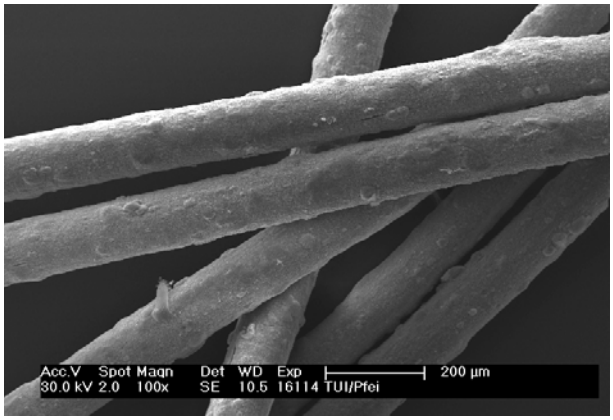

Fig. 7: SEM micrograph of fabricated cellulose fibers filled with undoped powder BHF10a, [1]

Fig. 7 shows an example of fabricated cellulose fibers filled with BHF 10a at a ratio of 1:5 (mass of cellulose : mass of ferrite powder). The diameter of the fibers amounts 108 µm. The magnetic properties will be transferred into the composites. Finally powder filled fibers for application as periodically magnetized flexible sensors for position detection are demonstrated in [1].
Other ways to use this powders for applications is to produce compounds of ferrite powder and other polymers. These powder filled polymers could be used as magnetic coating or as screen printing paste.

5 Summary

The investigations for the optimization of the undoped powders show, that a change in the melting temperature (from 1350 to 1400 °C) and longer crystallization times improve the magnetic properties of the powders by using constant crystallization temperatures of 840 °C. The combination of both positive effects could be part of further investigations. Furthermore it is shown, that the investigations for modifying the barium hexaferrite powders by La^{3+}/Co^{2+}-, Al^{3+}-, and Sr^{2+}-doping were only partially successful.

All dopings, except the full strontium substituted sample (Sr3a), show problems with the positioning of the doping ions inside the lattice of the powder. Thereby the powders contain only small parts of the expected doping amouts. The main part of the doping ions crystallizes inside the borate phase and will be lost after dissolving and separating. This is the reason that the magnetic properties of the doped samples did not have higher values for the saturation magnetization than the optimized undoped powders. The coercivity is increased by Al^{3+}-doped powder and the full strontium substituted sample. For further investigations the magnetic properties of the powders could be increased by using a reducing crystallization atmosphere for the La^{3+}/Co^{2+}-doping or using other crystallization conditions (time, temperature) for the Sr^{2+}-doped powders.

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References:

[1] Halbedel, B.; Hülsenberg, D.; Belau, S.; Schadewald, U.; Jakob, M.: Synthese und Anwendungen von maßgeschneiderten $BaFe_{12-2x}A^{II}_xB^{IV}_xO_{19}$-Pulvern. cfi/Ber. DKG 82 (2005) [13] 182-188

[2] Kools, F.; Morel, A.: LaCo-substituted ferrite magnets, a new class of high grade ceramic magnets; intrinsic and microstructural aspects. Journal of Magnetism and Magnetic Materials 242-245 (2002), 1270-1276

[3] An, S.Y.; et.al. : High magnetic performance in Al-substituted $BaFe_{12}O_{19}$ by wet chemical process. Phys. Stat. Sol. (c) 1 (2004), No. 12, 3310-3314

[4] Schadewald, U.: Untersuchungen zur bottom-up Kristallisation von modifizierten Bariumhexaferriten. Diplomarbeit, Technische Universität Ilmenau, 2005

[5] Knauf, O.: Nutzung großer Abkühlgeschwindigkeiten zum Amorphisieren spontan kristallisierender oxidischer Schmelzen, dargestellt am System $BaO\text{-}Fe_2O_3\text{-}B_2O_3$. Dissertation, Technische Universität Ilmenau, 1988

[6] Meister, F.; Vorbach, D.; Niemz, F.-G.; Schulze, T.; Träger, E.: High-Tech-Cellulose – Funktionspolymere nach dem ALCERU-Verfahren. Mat.-wiss. u. Werkstofftech. 34 (2003) 262-266

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