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Synthesis and characterization of A–Sn-substituted (A = Zn, Ni, Co) BaM–hexaferrite powders and ceramics

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Abstract

Aliovalently substituted BaM–hexaferrite powders with the composition $BaFe_{12-2x}Sn_xA_xO_{19}$ ($x = 0.1$–2.5) were prepared using the following techniques: solid-state reaction, high-energy milling, and chemical coprecipitation. The reaction temperature varied from 1300 °C to as low as 750 °C in the case of chemical coprecipitation. The saturation magnetization of the $BaFe_{12-2x}Sn_xA_xO_{19}$ powders varied between 66 and 4 emu/g and coercivity varied between 80 and 4400 Oe depending on their synthesis route, the substituted element A, and the substitution level x. BaM–hexaferrite ceramics were prepared by sintering at 1100–1400 °C for 2–6 h and their microstructure was characterized using electron microscopy.

Keywords: Ferrites; Magnetic properties; Milling; Powders-chemical preparation; Powders-solid state reaction

1. Introduction

BaM hexaferrite ($BaFe_{12}O_{19}$), also known as Ferroxdure, was developed in the Philips laboratories in the 1950s. Ferroxdure exhibits a very high coercivity, which makes it suitable for permanent magnets.[1] The magnetic properties of BaM hexaferrite can be tailored by the substitution of Ba^{2+} and/or Fe^{3+}. It is known that the large uniaxial crystalline anisotropy of BaM hexaferrite can be reduced by the Me–Ti- or Me–Sn- (Me = Zn, Co, Mn) substitution of Fe^{3+}, which is desirable for magnetic recording-media-applications.[2–9]

The composition and the microstructure both govern the magnetic properties of ferrites. As a result the preparation of ferrites is very important and has been investigated very intensively. The conventional solid-state technique involves high reaction temperatures and long milling times; however these conditions can be reduced by using other techniques, such as: chemical coprecipitation,[2,4,7] solid-state reaction via high-energy milling (also referred as mechanical alloying or ball milling),[5] and others.

In this study, A–Sn-substituted (A = Zn, Ni, Co) BaM–hexaferrite powders and ceramics with compositions of $BaFe_{12-2x}A_xSn_xO_{19}$ were prepared using the conventional solid-state technique, high-energy milling and chemical coprecipitation. The influence of composition and microstructure on the magnetic properties was investigated.

2. Experimental

Powder samples with the composition $BaFe_{12-2x}Sn_xA_xO_{19}$, A = Zn, Ni, Co and $x = 0.1$–2.5 were prepared by conventional solid-state reaction (SSR). The mixtures of the stohiometric amounts of $BaCO_3$, Fe_2O_3, SnO_2 and AO were homogenized and fired at 1300 °C for 3 h once or twice followed by 22–34 h wet milling in the iron mill. The particle size of the calcinates was measured by the granulometer Cilas HR-850-B

Another two series of samples with the composition $BaFe_{12-2x}A_xSn_xO_{19}$, A = Zn, Ni, Co and $x = 0.1$, 1.0 were prepared by high-energy milling (HEM) and chemical coprecipitation (CC). For the HEM method the mixtures of the stoichiometric amounts of $BaCO_3$, Fe_2O_3, SnO_2 and AO were homogenized and milled in Spex mill 8007 for 10 h with the powder to iron balls weight ratio equal to 1:5. The prereacted powder was pressed into pellets and fired at 1000–1300 °C for 6 h. The fired pellets were ground in an agate mortar.

For the CC method aqueous solutions from anhydrous $BaCl_2$, $FeCl_3$ and ACl_2 and a solution of

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anhydrous $SnCl_4$ in absolute ethanol were mixed in stochiometric amounts. The final solutions were precipitated with a NaOH solution at pH 13. The precipitates were filtered and washed with distilled water and absolute ethanol, dried at 80 °C and finally fired at 750 °C for 3 h.

The ceramics were sintered at 1100–1400 °C for 2–6h. For the microstructure examination the ceramics were polished and thermally etched at 1250 °C for up to 20 min. The composition of the powders and the ceramics was verified by X-ray diffraction (XRD) analysis using CuK_α radiaton with a Siemens D-5000 diffractometer and their microstructures were examined with a Jeol 840A SEM (scanning electron microscope) connected to a Tracor Northern Analyser for EDS (energy-dispersive) analysis. The particle size and crystal lattice parameters were determined using a corundum standard by a least square parameter approach and a computer program TopasR. The magnetic measurements were obtained with a Lake Shore 7312 vibrating-sample magnetometer. The maximum field of 1.2 T was sufficient to saturate the samples.

3. Results and discussion

X-ray diffractograms of the $BaFe_{11.8}Ni_{0.1}Sn_{0.1}O_{19}$ powders prepared by SSR at 1300 °C for 3 h, HEM at 1100 °C for 6 h and CC at 750 °C for 3 h are shown in Fig. 1. All of the observed diffractions in Fig. 1 correspond to BaM hexaferrite (PDF No. 74-1121) indicating that the powders are monophase. According to XRD analysis monophase samples were prepared by firing for 3–6 h at 1300 °C via SSR, for 6 h at 1000–1100 °C via HEM and for 3 h at 750 °C via CC. The reduction of the reaction temperature of the CC prepared samples compared with the other methods can be attributed to the much smaller particle size of the coprecipitated powders compared to the mixture of reactants for the SSR and HEM. Maximum particle size of the mixture of reactants for SSR, as-milled (HEM) and as-coprecipitated (CC) powders was of an order of μm, 100 nm and $<<100$ nm, respectively, as was observed by SEM. Correspondingly, diffractions of as-milled powders were much broader then those of the mixture of reactants for SSR. As for as-coprecipitated powders diffractions were not distinguishable at all, revealing that coprecipitates were very poorly crystallized.

In Fig. 2, lattice parameters of the $BaFe_{12-2x}A_xSn_xO_{19}$ powders prepared by SSR are shown. The bars in Fig. 2 indicate the experimental error. The unit cell is hexagonal and the space group of the BaM hexaferrite is $P6_3/mmc$. Both lattice parameters, a and c, increase with increasing substitution level (with increasing x). We can see that in terms of experimental error the lattice constants are linearly dependent on the substitution level. This can be explained by the larger ionic radii of Sn^{4+} and A^{2+} compared with Fe^{3+}.[10] The a parameters of the Co–Sn- and Zn–Sn-substituted materials determined in this study are slightly higher than some previously reported data.[4,6] This difference can be attributed to the different sample preparation methods if these methods influence the preferential site occupancy of the substituent ions. However, it is very unlikely that the unit cell of the substituted BaM hexaferrites would be smaller than that of pure $BaFe_{12}O_{19}$, as is the case in the previously reported data.[4,6] The agreement in the range of experimental error between the lattice parameters of the samples prepared by SSR and CC supports our results. Furthermore, the lattice constants of the $BaFe_{12-2x}Co_xSn_xO_{19}$ powders coincide with data for the $BaFe_{9.44}Co_{1.28}Sn_{1.28}O_{19}$ ($x=1.28$) single crystal.[11]

In Fig. 3, the saturation magnetization (Ms) and the coercivity (Hc) of the A–Sn-substituted BaM–hexaferrite powders and their dependence on composition is shown. In terms of better presentation the values corresponding to SSR samples are connected with lines. The Ms of the Co–Sn- and Ni–Sn-substituted samples decreases with the substitution level. This could be explained with preferential site occupancy of Sn^{4+} and A^{2+}. Fe^{3+} cations occupy seven octahedral (12k and 2a) sites and a trigonal (2b) site with spins in one direction, and two octahedral ($4f_{VI}$) and two tetrahedral ($4f_{IV}$) sites with spins in the opposite direction.[12] Although there are several possible preferential sites for Co^{2+} and Sn^{4+},[2,7,12] all possible combinations would result in a smaller magnetic moment and therefore lower the Ms of the Co–Sn-substituted samples compared with $BaFe_{12}O_{19}$. The Ni–Sn-substituted powders exhibited similar behaviour compared with the Co–Sn-substituted powders. Ni^{2+} and Co^{2+} have a smaller magnetic moment than Fe^{3+} and a similar ionic radius. Therefore, a similar magnetic structure for both types of powders is expected. On the other hand, the Ms of the Zn–Sn-substituted powders ($BaFe_{12-2x}Zn_xSn_xO_{19}$) prepared by SSR is approximately constant for $x \leqslant 1$ and decreases for $x>1$. Zn^{2+} has a strong preference for $4f_{IV}$ sites and the possible preferential site of Sn^{4+} is 2b with the opposite spin direction.[4] Since both Zn^{2+} and Sn^{4+} are diamagnetic no significant change in the Ms is expected. However, at a higher substitution level the Sn^{4+} also occupies other sites, such as $4f_{VI}$ and 12k, while only a small fraction of Zn^{2+} can be found at the 2b sites.[3,8] This could be a reason for the observed decrease of the Ms at higher substitution levels.

The $BaFe_{10.0}A_{1.0}Sn_{1.0}O_{19}$ powders with the same composition prepared by different methods exhibited different values of Ms (see Fig. 3). Assuming that the preparation method slightly modifies the preferential site occupancy of the substituents, this would modify the magnetic structure, too. This could be a reasonable

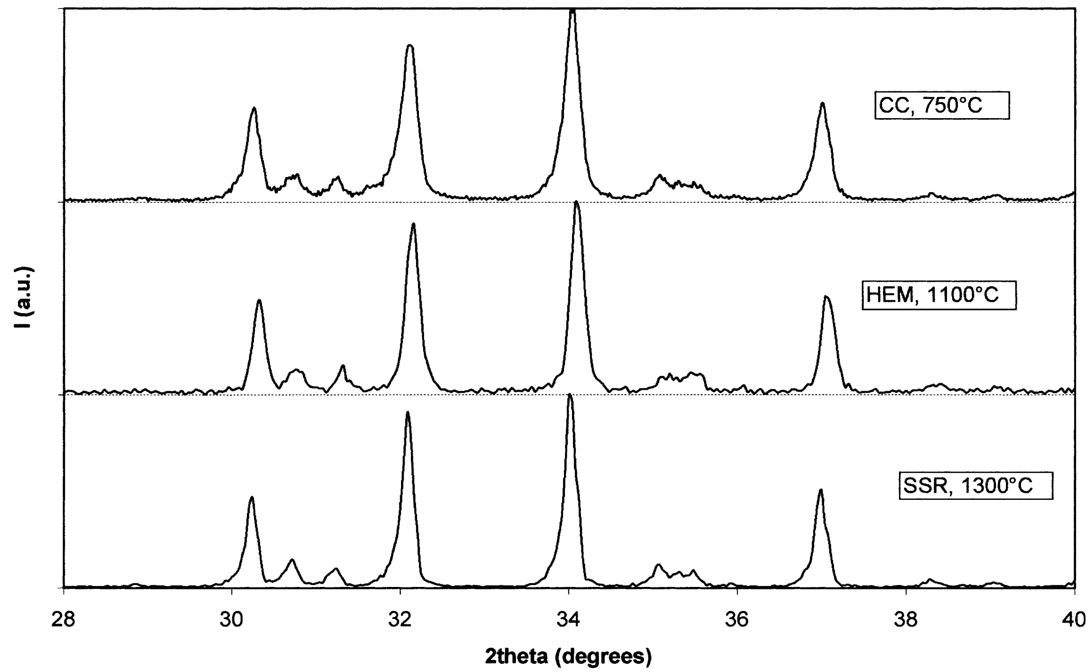


Fig. 1. X-ray diffractograms of the $BaFe_{11.8}Ni_{0.1}Sn_{0.1}O_{19}$ powders prepared by SSR, HEM and CC methods.

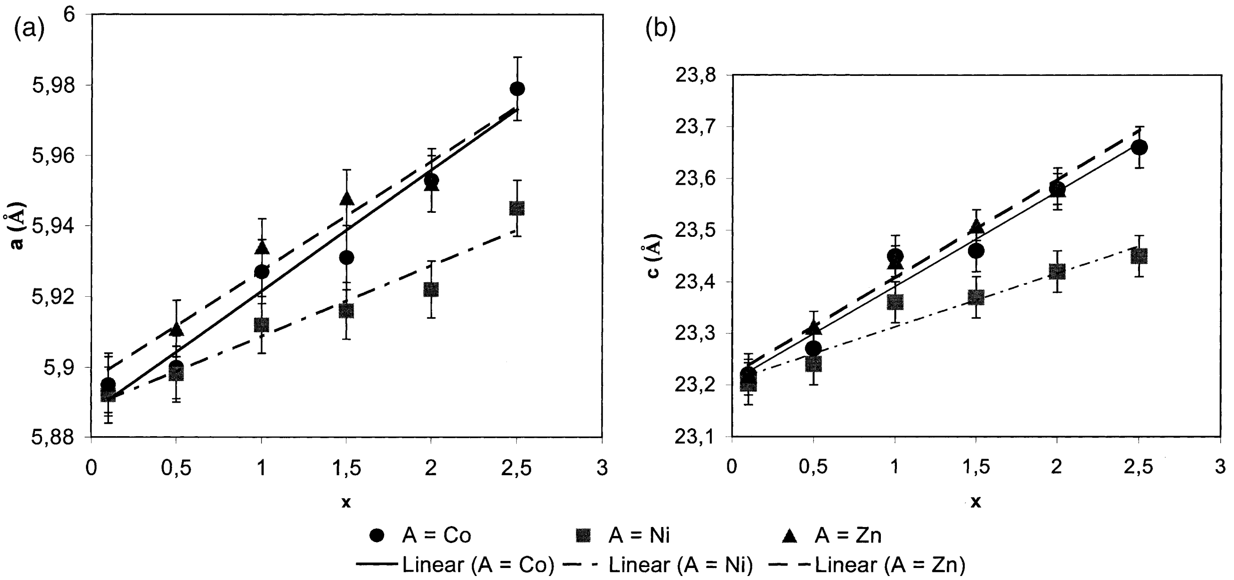
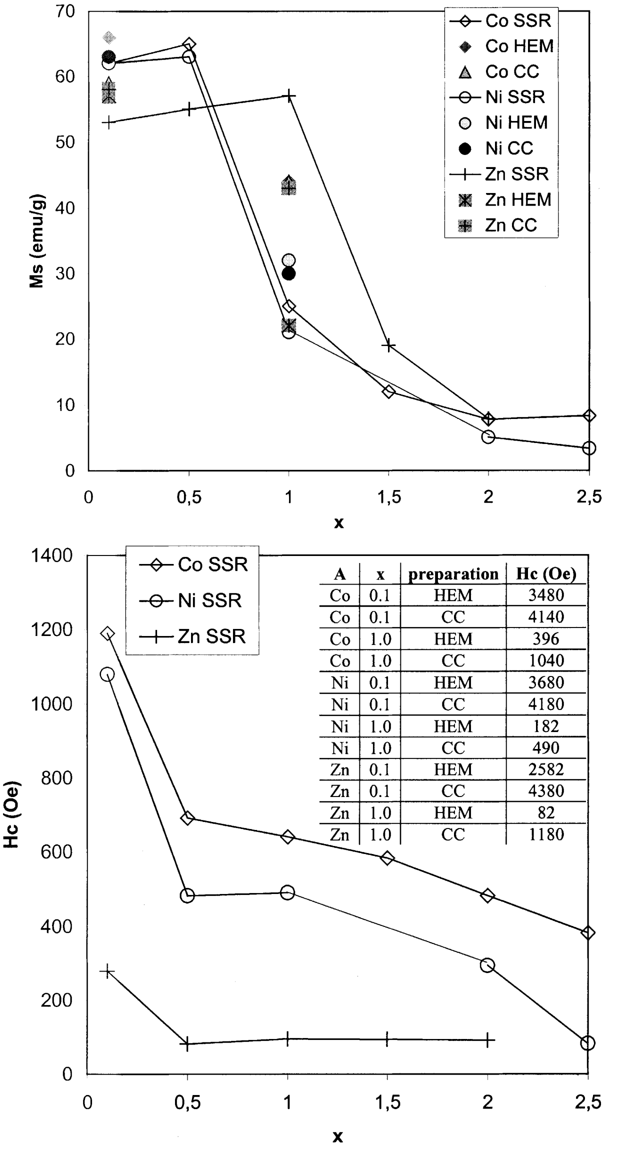


Fig. 2. Influence of the substitution level of the $BaFe_{12-2x}A_xSn_xO_{19}$ powders prepared by SSR at 1300 °C on the crystal lattice parameters.

explanation since the Ms for the lower substitution level ($BaFe_{11.8}A_{0.1}Sn_{0.1}O_{19}$) exhibited a similar Ms, regardless of the preparation method.

We can also see from Fig. 3 that the coercivity of the samples is decreasing with the substitution level. The coercivity of the BaM hexaferrites is dependent on the crystalline and the shape anisotropy. The crystalline anisotropy can be reduced by the substitution of the Fe^{3+} and finally changed from uniaxial to planar resulting in the Hc reduction. Lower values of Hc were measured for the Zn–Sn-substituted samples compared to the Co–Sn-substituted samples. The Hc of the Ni–Sn-substituted samples is similar to the Co–Sn-substituted samples. However, the shape anisotropy is influenced by the preparation procedure. We can see in the table inserted in Fig. 3 that the coercivity is the largest for the CC-prepared samples. This can be attributed to the smallest size of the CC-prepared particles compared to the others. The approximate particle diameter/thickness ratio determined by SEM and EDS analysis was 2/0.2 μm and 1/0.05 μm for HEM- and CC-prepared powders, respectively. The average particle size of the SSR-prepared powders determined by granulometry was approximately 7 μm.



A	x	preparation	Hc (Oe)
Co	0.1	HEM	3480
Co	0.1	CC	4140
Co	1.0	HEM	396
Co	1.0	CC	1040
Ni	0.1	HEM	3680
Ni	0.1	CC	4180
Ni	1.0	HEM	182
Ni	1.0	CC	490
Zn	0.1	HEM	2582
Zn	0.1	CC	4380
Zn	1.0	HEM	82
Zn	1.0	CC	1180

Fig. 3. Influence of the composition of the $BaFe_{12-2x}A_xSn_xO_{19}$ powders on the magnetic properties.

The ceramics sintered at 1400 °C for 2 h prepared from the SSR powders were not homogeneous. According to the EDS analysis two different phases can be identified. Both phases correspond to the BaM hexaferrite, with a slight variation in the composition. Compared with the nominal composition of $BaFe_{12-2x}Zn_xSn_xO_{19}$ one phase has a slight excess of Zn and the other phase has a slight deficit of Zn. When the SSR powders were sintered at 1300 °C for 3 h, the ceramics were very porous with a relative density <80%, although only one phase with the nominal composition was detected by the EDS analysis.

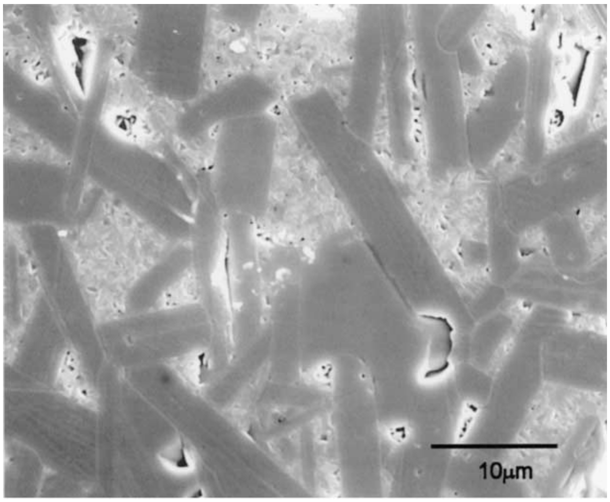


Fig. 4. SE micrograph of the thermally etched $BaFe_{10.0}Co_{1.0}Sn_{1.0}O_{19}$ ceramics prepared via CC and sintered at 1300 °C for 2 h.

In Fig. 4, is shown a SE micrograph of thermally etched polished ceramics surface with the composition $BaFe_{10.0}Co_{1.0}Sn_{1.0}O_{19}$ prepared via CC and sintered at 1300 °C for 2 h. During sintering, exaggerated grain growth occurred. In the micron-sized grain matrix grains of 10 μm and longer are included. The microstructure of the ceramics prepared by the HEM and sintered at 1300 °C for 6 h is similar to the one in Fig. 4, except that a smaller number of large grains can be observed. Besides that, the aspect ratio between the length and the thickness is smaller in the case of the ceramics prepared via CC. According to the EDS analysis the ceramics prepared via HEM or CC are monophase with the corresponded to the nominal composition.

4. Conclusions

A–Sn-substituted (A = Co, Ni, Zn) BaM–hexaferrite powders were prepared by three different methods: solid-state reaction at 1300 °C for 3–6 h, 10 h high-energy milling followed by firing at 1000–1100 °C for 6 h and chemical coprecipitation with NaOH at pH 13 followed by firing at 750 °C for 3 h. The formation temperature for the BaM hexaferrites was substantially decreased in the case of CC method. The magnetic properties of the powders varied with composition and preparation method. Nevertheless, the A–Sn-substituted BaM–hexaferrite powders prepared by CC and HEM exhibited magnetic properties suitable for magnetic recording applications.

Ceramics with a composition of $BaFe_{12-2x}A_xSn_xO_{19}$ were prepared from the powders by sintering at 1400 and 1300 °C for 2–6 h. Compositional inhomogeniety was detected in the ceramics prepared from the SSR powders and sintered at 1400 °C. This could be avoided by decreasing the sintering temperature. The microstructure of the monophase ceramics prepared from the HEM and CC powders by sintering at 1300 °C revealed the exaggerated grain growth of highly anisotropic grains. To obtain highly dense ceramics the sintering needs to be optimized.

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