Nanosize effects on the microstructure of BaFe$_{10.3}$Co$_{0.85}$Ti$_{0.85}$O$_{19}$ hexaferrite

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Nanosized and microcrystalline BaFe$_{10.3}$Co$_{0.85}$Ti$_{0.85}$O$_{19}$ samples were investigated by neutron diffraction. A strong anisotropy of the thermal expansion coefficient and its dependence on the grain size was established. The cation distributions and the magnetic moments were determined. The refined magnetic moments proved to be much lower than the theoretical spin only moments, especially for the 4e and 12k sites, indicating a local noncollinearity with short-range ordering.

Due to their large uniaxial magnetocrystalline anisotropy and strong Faraday rotation, barium hexaferrites are widely used as materials for permanent magnets, microwave devices, and recording media.$^{1,2}$ Recently, in order to achieve higher recording density with high signal to noise ratio the use of fine particle magnetic oxides, BaFe$_{12}$O$_{19}$ and its substituted derivatives in particular,$^{3}$ has attracted much interest. Surface and fine particle size effects on the technologically important properties of (Co$^{2+}$,Ti$^{4+}$) substituted Ba-hexaferrite have been recently investigated.$^{4,5}$ The typical features attributed to collective glassy state were revealed for nanocrystalline BaFe$_{10.4}$Co$_{0.8}$Ti$_{0.8}$O$_{19}$ particles$^6$ prepared by the glass crystallization method and in addition, the importance of strong interparticle interactions was concluded. However, there was no attempt to correlate the findings with possible changes in the core of the particles.

The aim of this work was to investigate the nanosize effects on the microstructure of (Co$^{2+}$,Ti$^{4+}$) doped Ba-hexaferrites by means of neutron diffraction. A nanosized and a microcrystalline sample with the composition of BaFe$_{10.3}$Co$_{0.85}$Ti$_{0.85}$O$_{19}$ were prepared by the soft chemistry method. The merit of this method of preparation$^7$ is that a narrow particle size distribution can be obtained and easily controlled over a wide range of sizes by appropriately guiding the process. The chemical composition was verified by scanning electron microscopy (SEM)-energy dispersive x ray analysis and SEM pictures were recorded for the preliminary characterization of the samples [see Figs. 1(a) and 1(b)].

Large agglomerates formed by the nanosized grains were observed indicating the presence of strong interparticle interactions.

The neutron diffraction measurements were carried out using the medium resolution high-intensity diffractometer the Budapest Neutron Centre ($\lambda$ = 1.0577 Å) and the high-resolution 3T2 diffractometer ($\lambda$ = 1.2251 Å) at LLB, Saclay at ambient temperature and at 10 K. The powder diffraction patterns were refined by the Rietveld method, using the program package Fullprof.$^8$

The crystal structure was described in the space group $P6_3/mmc$ of the prototype BaFe$_{12}$O$_{19}$ and the magnetic part of the scattering was generated adopting the Gorter-type collinear ferrimagnetic structure.$^9$ Line profile analysis showed that for the nanocrystalline sample there was a distinct particle shape effect manifested in a $\{hkl\}$ dependent broadening of the Bragg peaks, as it is displayed in Fig. 2. From the analysis of size dependent anisotropic broadening followed

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FIG. 1. Scanning electron microscopy images of (a) microcrystalline and (b) nanosized BaFe$_{10.3}$Co$_{0.85}$Ti$_{0.85}$O$_{19}$. 

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that the grains are platelet shaped with a mean diameter of 150±50 nm, and with the platelet vector being parallel to the hexagonal axes. For the platelet width, 14±5 nm was obtained.

The variation of the lattice parameters with temperature and grain size is remarkable (see Table I). From the room temperature values a reduction of the unit cell in the basal plain and its elongation along the hexagonal axis for the nanosized sample was established as compared to the microcrystalline one. This elongation vanishes at 10 K, while the contraction along the “a” lattice direction remains. The strong thermal crystallographic anisotropy and its dependence on composition of Ba-hexaferrites are known and repeatedly studied,10,11 because of the great importance in advanced thin films based devices.3 Assuming a temperature independent thermal expansion coefficient (\(\alpha\)) over the investigated temperature region 10–300 K, being far below the Curie point, the actual average values of \(\bar{\alpha}\) were calculated for both samples and are included in Table I. The large difference of the \(\bar{\alpha}\) parameters in the “c” direction is especially noteworthy. Another point of practical interest is, to compare our results with the corresponding data obtained in the literature, although they are differential and refer to a temperature region above room temperature, i.e., for pure BaFe\(_{12}\)O\(_{19}\).10 \(\bar{\alpha}_c = 12.2 \times 10^{-6} \text{ K}^{-1}\), \(\bar{\alpha}_a = 10 \times 10^{-6} \text{ K}^{-1}\), for Ba-hexaferrite doped with Ti\(^{4+}\) only,11 \(\bar{\alpha}_c = 9.5 \times 10^{-6} \text{ K}^{-1}\), \(\bar{\alpha}_a = 12.8 \times 10^{-6} \text{ K}^{-1}\). By applying our approach to the lattice parameters for BaFe\(_{12}\)O\(_{19}\) measured for the low temperature region,12 the order of magnitude remains unchanged, resulting in \(\bar{\alpha}_c = 13.6 \times 10^{-6} \text{ K}^{-1}\) and \(\bar{\alpha}_a = 12.6 \times 10^{-6} \text{ K}^{-1}\). The present study has shown that the (Co\(^{2+}\)+Ti\(^{4+}\)) substitution causes a significant lowering of the thermal expansion coefficient, and the grain size has an impact on the thermal expansion.

Previous investigations13,14 on microcrystalline material have shown that the distribution of Co\(^{3+}\)+Ti\(^{4+}\) ions on the five different ferric cation sublattices (2a, 4f\(_1\), 12k-octahedral, 4f\(_1\)-tetrahedral, 4e-half occupied bipyramidal) of the Ba-hexaferrite structure2 is complex. Because it might depend on the preparation technique the actual substitution rates of the different sites were determined for the present case. Average occupation factors (\(n_{i,av}\)) were determined for the five different sublattices, i, according to the relation: \(n_{i,av} \propto Fe = (n_{i,max} - n_{i,Ti} - n_{i,Co} b_{Co} + n_{i,Ti} b_{Ti}) / b_{Fe}\) where \(b_{Fe} = 9.45\), \(b_{Co} = 2.53\), and \(b_{Ti} = -3.438\) fm. In the refinements the chemical composition was fixed to \(\Sigma n_{i,Co} = \Sigma n_{i,Ti} = 0.85\) value. In addition, we used the Fe\(^{3+}\) magnetic form factor because the total amount of Co\(^{2+}\) is small as compared to the amount of Fe\(^{3+}\) ions. The results showed (see Table II) that the 2a site is occupied by Fe only, while all the other sublattices are partially substituted. In order to determine the distribution of different substituted cations over the remaining four sites physical assumptions have to be done. It is well known that the octahedral preference of an ion increases with its valence, thus it is reasonable to suppose that nonmagnetic Ti\(^{4+}\) ions occupy only octahedral (4f\(_1\),12k) sites.12 Consequently, the amount of Co\(^{2+}\) on the tetrahedral 4f\(_1\) and bipyramidal 4e positions could be calculated straightforward. For the occupancies of the octahedral sites we cannot give a unique solution, but considering the resultant linearly dependent solutions, we obtain limitations for the possible values.

For the investigated nano- and microcrystalline samples the cation occupation factors of the five sublattices proved to be the same within the error limits. The obtained values, however, are only in partial agreement with the corresponding ones for x = 0.85 extracted from the curves given in Ref. 14, which were plotted for different substitution ratios of samples prepared by the ceramic technology. The same holds for the sublattice magnetic moment values as well, as discussed in the following.

For both samples the refined local moments were close in value within the error limits and the respective site relevant value (see Table II) was substantially lower than for S-state Fe\(^{3+}\) ions (5 \(\mu_B\)), especially for the 4e and 12k sites.
where the moments point in the same direction. The formula
unit magnetization at 10 K ($M_{\text{f.u.}} = \sum \mu_{\text{site}} M_{\text{f.u.}}$) has parallel
orientation to the hexagonal axis but a smaller absolute value
($11 \pm 1.3 \mu_B$) as compared to that of pure BaFe$_{12}$O$_{19}$ ($20 \mu_B$).
A decreasing net magnetization with decreasing particle size
at a given substitution ratio could be expected to result
mainly from the increase of the ratio of spin-disordered
glassy volume to the total volume of the particles, as usually
interpreted. To seek reasoning in interparticle interference
effects, however, is not of relevance in powder diffraction
because of very rigorous requirements for lattice coherence
of positions and mutual orientation of the nanoparticles in
order to observe Bragg scattering. Also, the volume corre-
responding to a magnetically anomalous shell thickness typi-
cally estimated of the order of 1 nm was evaluated to give
rise of less than 4% scattered intensity. The obtained de-
creased magnetic moment values, therefore, should be a core
property and has to be explained by the specific cationic
distribution and resulting local noncollinearity of the mag-
netic properties both of the nano- and the microcrystal-
lite material. The decreased magnetic moments is a core property and finds explanation in the specific cationic
distribution and resulting local noncollinearity of the mag-
netic arrangement. Also, the ($\text{Co}^{2+}, \text{Ti}^{4+}$) substitution
causes a significant lowering of the thermal expansion coef-
ficient, and the grain size has an impact on the thermal ex-
pansion.

In conclusion, our present results demonstrate that the
preparation technique has a real impact on the crystalline and
magnetic properties both of the nano- and the microcrystal-
line material. For the nanoparticle size the average range of
atomic order and magnetic correlation coincide, and the core
has magnetization density approximately the same as that of
the microcrystalline material. The decreased magnetic mo-
mments is a core property and finds explanation in the specific cationic
distribution and resulting local noncollinearity of the mag-
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