Spin Reorientation in Substituted Barium Ferrite

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Abstract: The structural transformation of substituted hexagonal ferrite powders $\text{BaFe}_{10}\text{CoTiO}_{19}$ prepared by mechanical milling, was investigated as a function of grinding time by means of Mössbauer spectrometry and static magnetic measurements. A spin reorientation is clearly evidenced from the temperature dependence of the hyperfine parameters and of the initial magnetic permeability on the powder mechanically treated for 23h.

1. INTRODUCTION

Hexagonal ferrites always exhibit great technological interest as permanent magnets and high frequency devices. So, we investigated the electromagnetic properties of Co^{2+} and Ti^{4+} substituted baryum ferrite powders with various grain sizes, resulting from mechanical milling. It is well established that the effect of milling is not only to decrease the grain size but also to modify the crystalline and the microcrystalline structures and consequently the magnetic properties (see [1] for the strontium hexagonal ferrite). Indeed, the mechanical treatment first divides the powder grains into ultrafine particles, and then induces structural distortions preferentially located at the vicinity of the surface and at the boundaries of nanometric domains, leading to a nanostructured powders [2].

In the present study, the bulk material with chemical composition $\text{BaFe}_{10}\text{CoTiO}_{19}$, was reduced to small particles by dry ball milling, for different milling times (1h-2h-3h-6h and 23h). The crystallographic and magnetic transformations induced by ball milling are investigated by static magnetic measurements and Mössbauer spectrometry performed as a function of temperature.

2. RESULTS

Mössbauer experiments were carried out in transmission geometry over the temperature range 4.2K-650K, using a constant acceleration spectrometer and a ^{57}Co source diffused into a rhodium matrix. Three different regimes can be clearly distinguished from the temperature dependence of Mössbauer spectra recorded on $\text{BaFe}_{10}\text{CoTiO}_{19}$ powders mechanically treated for 23h: (i) below 150K, the spectra consist of magnetic sextets with rather well-resolved lines; (ii) for $150\text{K} < T < 620\text{K}$, the spectra can be decomposed in two components: a central paramagnetic doublet with a proportion which increases with the temperature and a broadened magnetic sextet; (iii) above $T = 620\text{K}$, the spectra reveal only the presence of pure electric hyperfine interactions. For $T < 150\text{K}$, the best fit requires the superimposition of four magnetic components: this description is consistent with the different iron sites present in the crystallographic structure. The values of the hyperfine fields are weakly reduced by comparison to those observed from the unmilled $\text{BaFe}_{10}\text{CoTiO}_{19}$ sample [3], this decrease may be attributed to the cationic distribution surrounding Fe nuclei, induced by the Co^{2+} and Ti^{4+} substitutions. Then, we concentrated on the analysis of spectra recorded in the intermediate temperature range ($150\text{K} < T < 600\text{K}$) because of their rather complex hyperfine structure. They were fitted with a continuous and discrete distribution of static hyperfine fields superimposed to a quadrupolar contribution. Finally, the temperature dependence of the average hyperfine field is plotted figure 1, including (a) or not (b) the paramagnetic contribution. Curve (b) clearly shows the presence of a cusp at $T \approx 220\text{K}$. The temperature dependence of the paramagnetic fraction is also plotted on figure 1 (c); let us note that we assume the same recoil free fraction f (Lamb-Mössbauer) factor for both magnetic and quadrupolar components.

MT (h)	0	1	2	3	6	23
Ms (uem/g)	68	63	60	57	52	36
Hc (Oe)	38	55	68	84	98	132

Table 1: Saturation magnetization Ms and coercive field Hc for applied magnetic fields of 20T and 0.35T, respectively measured at 300K, on BaFe₁₀CoTiO₁₉ powders, for different milling times MT.

Both saturation magnetization and coercive field were measured at 300K on BaFe₁₀CoTiO₁₉ powders mechanically treated for different times (see table 1): a strong decrease of the saturation magnetization and a large increase of the coercive field are observed with increasing grinding times. The temperature dependence of the initial magnetic permeability was measured on a toroidal powdered sample of BaFe₁₀CoTiO₁₉ mechanically treated for 23h and compared to that of the unmilled sample, as it is shown on figure 2. The low temperature maximum (Tr ≈ 250K) corresponds to a spin reorientation due to a change of magnetocrystalline anisotropy: below Tr, the uniaxial anisotropy is oriented along c axis, while above Tr, the planar anisotropy is perpendicular to c axis.

Figure 1: Temperature dependencies of the average hyperfine field for the BaFe₁₀CoTiO₁₉ powder after a mechanical milling of 23h, including (a) or not (b) the paramagnetic contribution and of the paramagnetic fraction (c).

Figure 2: Temperature dependence of the initial magnetic permeability of the BaFe₁₀CoTiO₁₉ powder before mechanical milling (a) and after a mechanical milling of 23h (b).

3. DISCUSSION

The hyperfine structure and magnetic characteristics described above are related to the nanostructured behaviour of the powder induced by the dry ball milling process. At low temperatures, the lowering of the average hyperfine field between unmilled and mechanically treated powders, is essentially due to the occurrence of disordered grain boundaries. In the intermediate temperature range, the cusp observed at ≈ 220K can be interpreted in terms of a spin reorientation, in agreement with initial magnetic permeability data. At higher temperatures, the progressive occurrence of a paramagnetic contribution is probably significant of both the existence of highly disordered or amorphous zones and the presence of superparamagnetic effects induced either by a distribution of nanocrystallites of different sizes, or by a superficial contribution. In order to check the existence of an amorphous phase, the powder mechanically treated for 23h was annealed during 24h at 1230°C. The 300K-Mössbauer spectrum is similar to that obtained on the unmilled powder, which is consistent with previous studies performed on mechanically milled strontium hexaferrite [1].

References

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