

Abstract

Magnetic properties of nanocrystalline Ba-Ferrite

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Nanocrystalline barium hexaferrite thin films and powders have been prepared by a water-based sol-gel method. Magnetic and structural properties of the barium ferrite were characterized with a x-ray diffraction, Rutherford backscattering spectroscopy(RBS), thermogravimetry(TG), differential thermal analysis(DTA), Fourier transform infrared spectroscopy(FT-IR), atomic force microscope(AFM), scanning electron microscope(SEM), and vibrating sample magnetometer(VSM) as well as Mössbauer spectroscopy.

Water-based coating sol for BaM was prepared using distilled water, methanol and glycerol as solution. The resulting precursor solutions were made at 0.2 M. *M*-type single phase is observed in the powder sample annealed at 950 °C in air for 6 h. The films were deposited by spin coating the stock solution on Si(100) a wafer with thermally oxidized SiO₂ layer and sapphire(001) substrate. The film with a thickness of 1800 Å were obtained by annealing the films at 600 – 900 °C in air for 2 hours. The pattern for the sample annealed at a temperature above 650 °C indexed well on the *M*-type hexagonal structure. It should be noted that no α -Fe₂O₃ and BaFe₂O₄ phase is detectable. The films were composed of uniformly distributed acicular-type grains, with diameters between 40 – 60 nm. Surface roughness of the films was between 2 and 4 nm. The perpendicular coercivity and in-plane one have the same value of 4.8 kOe. The film exhibits almost isotropic properties, which means the existence of a significant amount of in-plane *c*-axis orientation. This value seems to be suitable for high-density recording

media. The coercivity increased monotonously with increasing annealing temperature in the films annealed in air. The perpendicular coercivity squareness S^* , a measure of the slope of the loop at H_C , is 0.65.

BaFe₁₂O₁₉ thin film was epitaxially grown on single crystalline sapphire(001) substrate with [BaM(00l)/sapphire(00l)] relation. The full width at half maximum of the rocking curve of (008) peak is 0.28°. The AFM was used to detect the grain size and surface morphology. Surface roughness of the films was between 2 and 4 nm. The perpendicular and in-plane coercivities are 4.9 and 4.7 kOe, respectively, at room temperature under an applied field 15 kOe. The magnetization hysteresis loops are almost the same for magnetic fields both applied in parallel and perpendicular. The film exhibits almost isotropic properties, which means the existence of a significant amount of in-plane *c*-axis orientation. However, it is not clearly shown in the x-ray spectrum. Since the *c*-axis in-plane oriented grains have no preferred orientation in their basal plane, there is no specific set of crystal planes which must be parallel to the film plane. By the law of approach to saturation(LAS) the effective anisotropy field H_A and crystalline anisotropy constant K_1 were estimated. The value of K_1 and H_A were $K_1=2.70 \times 10^6$ erg/cm³ and 14.6 kOe, respectively and this is comparable to the reported bulk value of $K_1=3.30 \times 10^6$ erg/cm³ measured at room temperature. Rutherford backscattering spectroscopy confirmed the excellent stoichiometry of the film and bulk. The composition was confirmed to be Ba:Fe:O=1.0:12.0:19.0.

Co-Ti substituted *M*-type hexagonal barium ferrite nanoparticles BaFe_{12-2x}Co_xTi_xO₁₉ have been prepared by a sol-gel method. The result of x-ray diffraction (XRD) measurements shows that the *a*, *c* lattice parameters increase with increasing *x* from $a=5.822$ Å, and $c=23.215$ Å for *x*=0.0, to $a=5.895$ Å, $c=23.295$ Å for *x*=1.0. The ⁵⁷Fe Mössbauer spectra were fitted by a least-squares technique with four subpatterns of Fe sites in the structure and corresponding to the $4f_2$, $2a+4f_1$, $12k$, and $2b$ site. The relative spectra areas of BaFe₁₀CoTiO₁₉ at room temperature were 15, 27, 50, and 8 % for $4f_2$, $2a+4f_1$, $12k$, and $2b$ subpatterns, respectively. The $2b$ site had a very large quadrupole splitting. The isomer shifts indicated that the valence states of the Fe ions were ferric. The magnetization slightly decreases and the coercivity H_C , drops dramatically from about 5,014 to 228 Oe as *x* increases from 0.0 to 1.0. Co-Ti substituted barium hexaferrite to be controlled to reduce their coercivities without a decrease of their magnetization. The substitution

of Co^{2+} and Ti^{4+} will weaken the exchange interaction between the iron ions and lead to a reduction in the Curie temperature with increasing x as observed.

By substituting Fe^{3+} substituting in $\text{BaFe}_{12}\text{O}_{19}$ by Cr^{3+} , we have been able to attribute the Mössbauer parameters to the 5 crystallographic sites ($4f_2$, $2a$, $4f_1$, $12k$, and $2b$) of the structure. Only the octahedral sublattices were occupied by Cr ions. The isomer shifts indicate that the valence state of the Fe ions was Fe^{3+} . The Curie temperatures of $\text{BaFe}_{12-x}\text{Cr}_x\text{O}_{19}$ decreased linearly increasing Cr substitution, at a rate of 55K/Cr atom. This implies that the $\text{Fe}^{3+}\text{-O-Cr}^{3+}$ superexchange interaction in $\text{BaFe}_{12-x}\text{Cr}_x\text{O}_{19}$ is weaker than the $\text{Fe}^{3+}\text{-O-Fe}^{3+}$ superexchange interaction. By substituting Cr^{3+} for Fe^{3+} , it is concluded that Cr^{3+} strongly affects the decrease of both the Curie temperature and the magnetization.

$\text{BaFe}_{11.9}\text{Mn}_{0.1}\text{O}_{19}$ powders were prepared by a sol-gel method. X-ray diffraction showed that the $\text{BaFe}_{11.9}\text{Mn}_{0.1}\text{O}_{19}$ had a M -type hexagonal structure with $a=5.900$, $c=23.219$. Mössbauer spectroscopy was performed at various temperatures ranging from 13 to 800 K, and each spectrum for a temperature below the Curie temperature was fitted with five subspectra of Fe sites in the structure ($4f_2$, $2a$, $4f_1$, $12k$, and $2b$). The area fractions of the subspectra at 13 K were 18.0 %, 10.2 %, 17.5 %, 46.1 %, and 8.2 %, respectively. The $2b$ site had a very large quadrupole splitting. The isomer shifts indicated that the valence state of the Fe ions was ferric. The saturation magnetization M_S was 58 emu/g, and coercivity H_C was 5,141 Oe at room temperature under an applied field of 15 kOe. The Curie temperature decreases with Mn concentration at a rate 50 K/Mn atom. This implies that $\text{Fe}^{3+}\text{-O-Mn}^{3+}$ superexchange interaction in $\text{BaFe}_{11.9}\text{Mn}_{0.1}\text{O}_{19}$ is weaker than $\text{Fe}^{3+}\text{-O-Fe}^{3+}$ superexchange interaction.