Effect of annealing in low PO_2 on the structure and magnetic properties of M-type Sr-hexaferrite

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M-type Sr-hexaferrites are one of the most utilized materials in permanent magnets due to their low price, outstanding chemical stability, and characteristic hard magnetic properties. [1] It has been shown that Ca-La-Co [2] substitutions are one of the most successful approaches, leading to significant enhancement in the crystalline anisotropy without reducing the M_S. In this research, the effects of annealing atmospheres, air and N_2 on the crystalline phase, microstructure, and magnetic properties are comparatively studied for the non-substituted SrM and the Ca-La-Co-substituted SrM. The correlations of the cation substitution ratio of $[La^{3+}]/[Co^{2+}]$, phase stability, and formation of oxygen vacancy are discussed. It is also clearly revealed that the effect of oxygen vacancy on the magnetic properties of the M-type Sr-hexaferrites through thin film experiment.

Non-substituted SrM ($SrFe_{12}O_{19}$) and La-Co substituted SrM ($Sr_{0.7}La_{0.3}Fe_{11.7}Co_{0.3}O_{19}$) and La-Ca-Co substituted SrM ($Sr_{0.1}Ca_{0.45}La_{0.45}Fe_{11.7}Co_{0.3}O_{19}$) samples were prepared by conventional solid state reaction process. The SrM thin film with thickness of 130 nm was prepared on Si/SiO_2 substrate by pulsed laser deposition (PLD) and subsequent ex-situ annealing process at 970°C in air. Ex-situ annealing on the films was performed in the vacuum at 300-500°C for 1h. Analysis by X-ray diffraction and field emission scanning electron microscopy (FE-SEM) were performed for phase identification and microstructural observation, respectively. Magnetic hysteresis curves were measured using a physical property measurement system-vibrating sample magnetometer at room temperature (300 K) with sweeping magnetic field within ± 5 T.

During annealing in N_2 at 1200°C, the Ca-La-Co-substituted SrM decomposed to the three different ferrite phases of orthorhombic, spinel, and hexagonal structures while non-substituted SrM and La-Co SrM maintained the M structure as the primary phase. It is suggested that the charge-imbalance substitution of La^{3+} - Co^{2+}, with the ratio of $[La^{3+}]/[Co^{2+}]$ = 1.5 induces the phase instability of the hexaferrite structure, which cause oxygen vacancy formation and subsequent phase transformation during the low PO_2 annealing. In the thin film experiment, polycrystalline $SrFe_{12}O_{19}$ (t = 130nm) films were prepared on the SiO_2/Si substrate by pulsed laser deposition and post-annealing processes. After annealing in vacuum at 500°C, the films showed 80% increased magnetization value at the applied magnetic field of H = 15 kOe with a significantly reduced coercivity without microstructural change. The softer magnetization behavior with the increased MS over the theoretical limit of SrM is attributed to the formation of oxygen vacancies in the hexagonal structure, which is accompanied with Fe valence change from Fe^{3+} to Fe^{2+}.

References

[1] J. J. Went, G. W. Rathenau, E. W. Gorter, G. W. van Oosterhout, Ferroxdure, A Class of Permanent Magnetic Materials, Philips Tech. Rev. **13**, (1952) 194-208

[2] Y. Kobayashi, S. Hosokawa, E. Oda, S. Toyota, Magnetic properties and composition of Ca-La-Co M-type ferrites, J. Jpn. Soc. Powder Metall. 55 (2008) 541-546.