Structure and Magnetic Properties of M-Type Sr-Hexaferrite with Ca, La Substitutions

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Abstract : M-type Sr-hexaferrite (SrFe12O19) have been studied during the past decades because it is the most utilized materials in permanent magnets due to their low price, outstanding chemical stability, and appropriate hard magnetic properties. Many attempts have been made to improve the intrinsic magnetic properties of M-type Sr-hexaferrites (SrM), such as by improving the saturation magnetization (MS) and crystalline anisotropy by cation substitution. It is well proved that the Ca-La-Co substitutions are one of the most successful approaches, which lead to a significant enhancement in the crystalline anisotropy without reducing MS, and thus the Ca-La-Co-doped SrM have been commercialized in high-grade magnet products. In this research, the effect of respective doping of Ca and La into the SrM lattices were studied with assumptions that these elements could substitute both of Fe and Sr sites. The hexaferrite samples of stoichiometric SrFe₁₂O₁₉ (SrM) and the Ca substituted SrM with formulae of $Sr_{1-x}Ca_xFe_{12}O_a$ (x = 0.1, 0.2, 0.3, 0.4) and $SrFe_{12-x}Ca_xO_a$ (x = 0.1, 0.2, 0.3, 0.4), and also La substituted SrM of $Sr_{1-x}La_xFe_{12}O_a$ (x = 0.1, 0.2, 0.3, 0.4) and $SrFe_{12-x}La_xO_a$ (x = 0.1, 0.2, 0.3, 0.4) were prepared by conventional solid state reaction processes. X-ray diffraction (XRD) with a Cu K α radiation source (λ =0.154056 nm) was used for phase analysis. Microstructural observation was conducted with a field emission scanning electron microscopy (FE-SEM). M-H measurements were performed using a vibrating sample magnetometer (VSM) at 300 K. Almost pure M-type phase could be obtained in the all series of hexaferrites calcined at > 1250 °C. Small amount of Fe₂O₃ phases were detected in the XRD patterns of $Sr_{1-x}Ca_xFe_{12}O_a$ (x = 0.2, 0.3, 0.4) and $Sr_{1-x}La_xFe_{12}O_a$ (x = 0.1, 0.2, 0.3, 0.4) samples. Also, small amount of unidentified secondary phases without the Fe₂O₃ phase were found in the samples of $SrFe_{12-x}Ca_xOa$ (x = 0.4) and $SrFe_{12-x}La_xOa$ (x = 0.3, 0.4). Although the Ca substitution (x) into SrM structure did not exhibit a clear tendency in the cell parameter change in both series of samples, Sr_{1-x}Ca_xFe₁₂O_a and SrFe_{12-x}Ca_xO_a , the cell volume slightly decreased with doping of Ca in the Sr_{1-x}Ca_xFe₁₂O_a samples and increased in the SrFe_{12-x}Ca_xO_a samples. Considering relative ion sizes between Sr²⁺ (0.113 nm), Ca²⁺ (0.099 nm), Fe³⁺ (0.064 nm), these results imply that the Ca substitutes both of Sr and Fe in the SrM. A clear tendency of cell parameter change was observed in case of La substitution into Sr site of SrM (Sr1-xLaxFe12Oa); the cell volume decreased with increase of x. It is owing to the similar but smaller ion size of La^{3+} (0.106 nm) than that of Sr^{2+} . In case of $SrFe_{12-x}La_xO_a$, the cell volume first decreased at x = 0.1 and then remained almost constant with increase of x from 0.2 to 0.4. These results mean that La only substitutes Sr site in the SrM structure. Besides, the microstructure and magnetic properties of these samples, and correlation between them will be revealed.

Keywords : M-type hexaferrite, substitution, cell parameter, magnetic properties

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