Phase Separation of Epsilon Iron Oxide and Barium Ferrite using a Reverse-Micelle and Sol-Gel Combined Synthesis

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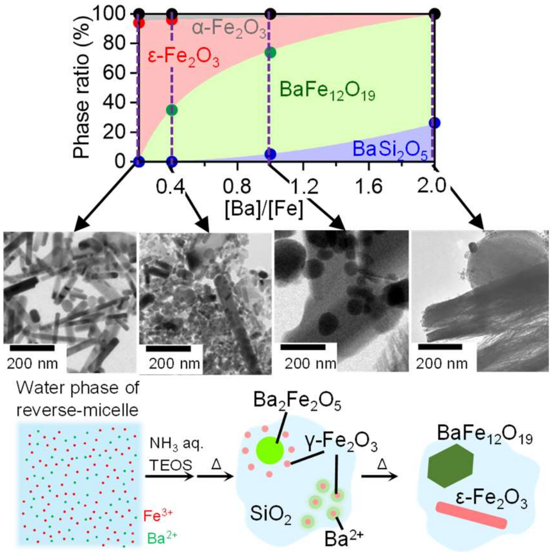
Hard magnetic ferrites, epsilon iron oxide (ε-Fe_2O_3) and barium ferrite ($BaFe_{12}O_{19}$) are of significant interest due to their magnetic properties and potential applications in magnetic recording media and millimetre-wave absorption. This study investigates the effect of barium ion (Ba^{2+}) to iron ion (Fe^{3+}) ratio on the synthesis of ε-Fe_2O_3 and $BaFe_{12}O_{19}$ using a combined reverse-micelle and sol-gel technique.[1,2] Reverse-micelle solutions were prepared containing $Fe(NO_3)_3$ and varying concentrations of $Ba(NO_3)_2$ (solution A), or ammonium hydroxide (solution B). Solution B was added dropwise into solution A, followed by tetraethyl orthosilicate and stirring, yielding a precipitate that was collected, annealed at 1000°C, and etched with NaOH (aq) and HCl (aq) to remove the silica matrix. By varying the Ba/Fe molar ratio, distinct phase separations and morphological changes were observed. At low Ba ion concentrations ([Ba]/[Fe] = 0.2), ε-Fe_2O_3 nanorods form predominantly, whereas higher Ba concentrations ([Ba]/[Fe] ≥ 0.4) favour the formation of $BaFe_{12}O_{19}$, shown by microscopy and powder X-ray diffraction (PXRD). At an equimolar ratio ([Ba]/[Fe] = 1), ε-Fe_2O_3 and $BaFe_{12}O_{19}$ coexist in equal proportions, with no intermediate phases. Magnetic behaviour shows reduced coercive field and increased magnetic saturation as the major phase shifts from ε-Fe_2O_3 to $BaFe_{12}O_{19}$ as the Ba ion ratio is increased.



Based on the analysis conducted using scanning transmission electron microscopy coupled with energy dispersive X-ray spectroscopy and PXRD, the following mechanism is proposed for the sintering process: At 1000 °C, in areas of high barium ion concentration, γ-Fe_2O_3 nanoparticles interact with $Ba_2Fe_2O_5$ to form $BaFe_{12}O_{19}$. Conversely, in areas of low barium ion concentration, γ-Fe_2O_3 nanoparticles undergo transformation into ε-Fe_2O_3 nanorods. This study clarifies the influence of the Ba/Fe ion ratio on this synthesis, facilitating the targeted production of ferrite materials for advanced magnetic and technological applications.

1) J. MacDougall, H. Tokoro, M. Yoshikiyo, A. Namai, S. Ohkoshi, *Eur. J. Inorg. Chem.*, **2024**, *27*, e202400148. 2) J. Jin, S. Ohkoshi, K. Hashimoto, *Adv. Mater.* **2004**, *16*, 48.

