FORMATION MECHANISM OF BaFe$_{12}$O$_{19}$ NANOPARTICLES PROCESSED VIA WET CHEMICAL ROUTE USING MIXED SOLVENT

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Nanosize particles of barium hexaferrite were prepared by co-precipitation route using solution of iron and barium chlorides with a Fe$^{3+}$/Ba$^{2+}$ molar ratio of 11. Water and a mixture of water/ethanol with volume ratio of 1:3 were used as solvents. Co-precipitated powders were calcined at various temperatures. XRD results showed that single phase barium hexaferrite forms at 900°C for sample synthesized in aqueous solution and its formation is resulted from the reaction between mainly crystalline phases, while this temperature decreased to 700°C for sample synthesized in water/ethanol solution and the formation of barium hexaferrite consists of reactions between amorphous phases with crystalline phases. SEM micrographs of the calcined samples at 800°C indicated that the morphology of particles was affected by the type of solvent. Nano size particles of barium hexaferrite with mean particle size of almost 80 nm were observed in the SEM micrograph of sample synthesized in water/ethanol solution after calcination at 800°C. Barium hexaferrite crystallites with mean size of 35 nm, which was approximately consistent with size obtained from XRD line broadening technique, could be seen in TEM image of this sample after calcination at 700°C.

*Key words: Barium hexaferrite; nano-particles; co-precipitation.

1. Introduction

Barium hexaferrite magnetic material has significant potential for applications such as permanent magnets and microwave absorbing coatings, because of the adequate combination of high Curie temperature, high coercivity, chemical stability and resistance to corrosion. Fine BaO.6Fe$_2$O$_3$ particles also exhibit suitable properties for perpendicular magnetic recording media.

Barium ferrite is produced mainly by a conventional mixed oxide ceramic method which involves the calcining of BaCO$_3$ and $\alpha$-Fe$_2$O$_3$ mixtures at around 1200°C. However, in order to improve the material properties, several non-conventional routes such as co-precipitation, hydrothermal, micro-emulsion, glass crystallization and sol–gel methods have also been employed to synthesize barium ferrite. Among these methods, co-precipitation is the most attractive due to simple operation and ease of mass production.

The use of a mixed solvent is a new approach in nanomaterials synthesis and processing. Ethanol (CH$_3$CH$_2$OH) is a polar solvent which is miscible with water at any ratio, and the addition of ethanol to water can easily change its physicochemical properties. The objective of the present study is to investigate the influence of using 75 vol. % ethanol as a co-solvent along with water on the formation mechanism, crystallite size and morphology of barium hexaferrite particles obtained by co-precipitation method.
2. Experimental Procedure

FeCl₃·6H₂O (Merck, > 99%) and BaCl₂·2H₂O (Merck, ≥ 99%) with a Fe/Ba molar ratio of 11 were dissolved in water and a mixture of ethanol/water with a volume ratio of 3:1. The molar ratio of Fe/Ba was 11 to maintain the stoichiometry of the product due to the poor solubility of Ba⁺² cations in water. Two prepared solutions were co-precipitated by addition of NaOH with OH⁻/Cl⁻ molar ratio of 2 at room temperature. The samples synthesized in water and ethanol/water solutions were washed by distilled water and ethanol, respectively and dried at 70°C for 15 h. The dried powders were then annealed at various temperatures for 1 h in air to obtain barium ferrite magnetic phase. The samples synthesized in ethanol/water and water solutions are named for brevity “EtOH” and “W”, respectively.

The phase identification of the specimens was performed using X-ray diffraction (XRD) on a Philips PW3170 X-ray diffractometer using Co-Kα radiation.

The mean crystallite size of BaFe₁₂O₁₉ annealed powders was calculated from the X-ray peak broadening of three diffraction peaks related to (107), (114) and (220) planes (the most intense XRD peaks) using the classical Scherrer equation.

CamScan MV2300 scanning electron microscopy was used to characterize the particles morphology. The microstructure of the powder after annealing was observed using a transmission electron microscope (TEM, CM200 Philips).

3. Results and Discussion

Figure 1 shows the X-ray powder diffraction patterns for the co-precipitated precursors. It appears that the powders are amorphous with some poorly crystallized material. The wide peaks correspond to the barium carbonate. Formation of BaCO₃ is probably due to the loss of water from the amorphous precursors during the drying. It means that since the samples are exposed to air for several hours during the drying, BaCO₃ crystallized from the Ba-precursor and CO₂ absorbed from the air.

However, the wider and less distinctive of BaCO₃ peaks related to the EtOH precursor than the W precursor show the finer and more amorphous nature of powders obtained from the diethylene glycol solution.

XRD patterns of the W sample after annealing at various temperatures are shown in Fig. 2. XRD pattern of the W sample annealed at 650°C consists of amorphous phase as well as peaks related to the crystalline phases such as barium carbonate and hematite. At 700°C, barium carbonate decomposed and simultaneously barium monoferrite phase is formed. Also, reflections of barium hexaferrite could be observed in the diffraction pattern of this sample. Barium hexaferrite became the major phase in sample annealed at 750°C, but some un-reacted intermediate phases like barium monoferrite and hematite still observed.

Remaining of phase impurities up to 850°C indicates the poor reactivity of the hard agglomerated precursor co-precipitated from the water solution which retarded the diffusion of Ba²⁺ and hence formation of barium ferrite. Single phase barium hexaferrite was obtained at 900°C via completion of solid state reaction between intermediate crystalline phases.

Figure 3 shows the X-ray powder diffraction patterns for the EtOH sample after it was annealed at various temperatures for 1 h. XRD pattern of the EtOH sample annealed at 600°C indicated that barium carbonate was decomposed at this temperature.

![Fig. 1. X-ray diffraction patterns for the precursors dried at 70°C: (a) W precursor, (b) EtOH precursor.](image-url)
without formation of barium monoferrite as an intermediate crystalline phase. Furthermore, barium hexaferrite became the major phase at this temperature. Reaction of barium carbonate with amorphous phase containing Fe$^{3+}$ ions can be predominant mechanism for formation of barium hexaferrite till 600°C. A minor hematite peak at 650°C indicates that the sample is not single phase. Barium hexaferrite was fully formed at a relatively low temperature of 700°C by reacting hematite and amorphous phase containing Ba$^{2+}$ ions. It is concluded that using ethanol as a co-solvent along with water significantly lower the formation temperature of magnetic phase.

Figure 4 shows SEM micrograph of the W sample after annealing at 800°C. The mean particle size was measured as 150 nm for this sample.

Figure 5 shows SEM micrograph of the EtOH sample after annealing at 700°C. The mean particle size was measured as 50 nm for this sample.

It is noted that different physical and chemical properties of ethanol and water can remarkably influence the co-precipitation process. In aqueous co-precipitation, water molecules can bridge the surface hydroxyl groups of neighboring precipitates to form hard agglomerates by making solid necks between precipitate small particles as long as they nucleated. Therefore, the powders treated in water prefer to form large particles.

Fig. 2. X-ray diffraction patterns for W sample after annealing at various temperatures for 1 h.

Fig. 3. X-ray diffraction patterns for EtOH sample after annealing at various temperatures for 1 h.

Fig. 4. SEM micrograph of the W sample annealed at 800°C for 1 h.
In contrary, ethanol is postulated to hydrogen bands to surface hydroxyls, but could not cause particle-particle interaction and hence particle coarsening.\textsuperscript{8} Thus, the powders prepared in ethanol/water mixture showed softer agglomeration nature and smaller mean particle size leading to the precursor becoming very soft and friable.

Barium hexaferrite crystallites with mean size of 35 nm, which is approximately consistent with size obtained from XRD line broadening technique, could be seen in TEM image of EtOH sample annealed at 700\textdegree C (Fig. 6).

Since the bonding of amorphous nano-particles in precursor is rather weak, it is easier to break these bonds through heating during annealing treatment. Therefore, the EtOH precursor is more suitable for low temperature formation of barium ferrite than W precursor.

4. Conclusion
Nano size particles of barium hexaferrite have been synthesized at a relatively low temperature of 700\textdegree C by co-precipitation method using ethanol/water mixture solution of iron and barium chlorides with a Fe/Ba molar ratio of 11. Note that the formation temperature of barium hexaferrite was 900\textdegree C for sample processed in aqueous solution.

It is believed that ethanol properties such as ability to weakening the hydrogen bands between the adjacent particles and its low surface tension are effective in the synthesizing more amorphous and smaller size of particles in the ethanol/water mixed solvent and following low formation temperature of barium ferrite.

References