

Crystallization of *M*-type hexagonal ferrites from mechanically activated mixtures of barium carbonate and goethite

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Abstract. *M*-type hexagonal ferrite precursor was prepared by a soft mechanochemical treatment of BaCO₃ and α -FeOOH mixtures. The effect of milling on its structure and thermal behaviour was examined by XRD, SEM and FTIR. Well crystallized *M*-type hexagonal ferrite was formed from just 1 h milled precursors at 800°C. The beneficial effect of milling was explained in terms of increased homogeneity with simultaneous hetero bridging bond formation between powder constituents.

Keywords. *M*-type hexagonal ferrite; mechanical activation; powder; crystallization.

1. Introduction

Hexagonal ferrite, BaFe₁₂O₁₉ (*M*-phase), is widely studied as a permanent magnet and more recently for high-density magnetic recording media. Many synthesis techniques, such as solid state reaction (Steier *et al* 1999), co-precipitation (Ogasawara and Oliveira 2000; Janasi *et al* 2002), combustion (Huang *et al* 2003), have been exploited. Mechanochemical method is one of the interesting methods for the preparation of *M*-phase. There are several reports on this subject (Subrt and Tlaskal 1993; Ding *et al* 1998; Liu *et al* 2000; Mendoza-Suarez *et al* 2001). From mechanically activated mixtures, crystallization of *M*-phase usually occurs between 800 and 1200°C and shows nano or submicron size. However, mechanical milling is a high energy consuming process, which requires additional equipment such as high energy shaker mill (Ding *et al* 1998; Liu *et al* 2000).

Subrt and Tlaskal (1993) have described that if starting mixture contains hydroxyl containing compounds the crystallization of *M*-phase occurs at 800°C. They have attributed this reaction to the appearance of a highly reactive iron oxide formed during dehydration of iron hydroxides.

We have previously reported that a soft-mechanochemical reaction has a great potential for the synthesis of hexagonal ferrites such as *Y*-phase (Ba₂Co₂Fe₁₂O₂₂) (Te-

muujin *et al* 2004). We found that the existence of the hydroxyl containing compounds in the raw materials does not guarantee an improved solid state reaction rate of the powder constituents. Soft-mechanochemical reaction takes place during the milling of water or hydroxyl containing compounds because of their easy polarization of the surface hydroxyl groups and allows obtaining of precursors containing hetero bridging bonds between the metallic species by relatively mild mechanical stresses. The aim of the present research is to characterize the reaction mixture of the mechanically treated hydroxyl containing compounds and to evaluate its crystallization behaviour during heat treatment.

2. Experimental

The starting reagents were goethite α -FeOOH (GNA-85N, with 0.2 μ m long needle like morphology) from Toda Kogyo Corp. and BaCO₃ (0.2 μ m long rod like morphology), both with analytical grade purity. A stoichiometric mixture for *M*-phase was activated with multi-ring type mill, Mechano Micros[®] (Nara Machinery) for 1 and 4 h. The rates of revolution and counter-revolution of the rotor and the vessel were fixed at 1250 and 250 min⁻¹, respectively. A 30 g of the powder, corresponding to 15% of the effective volume of the vessel, was charged for activation. After milling, samples were calcined at 600, 800 and 1000°C in air.

Samples were characterized by a powder X-ray diffractometry (Rigaku RINT 2000), FTIR (Bio-Rad Win-IR) and FE-SEM (Hitachi S-4000).

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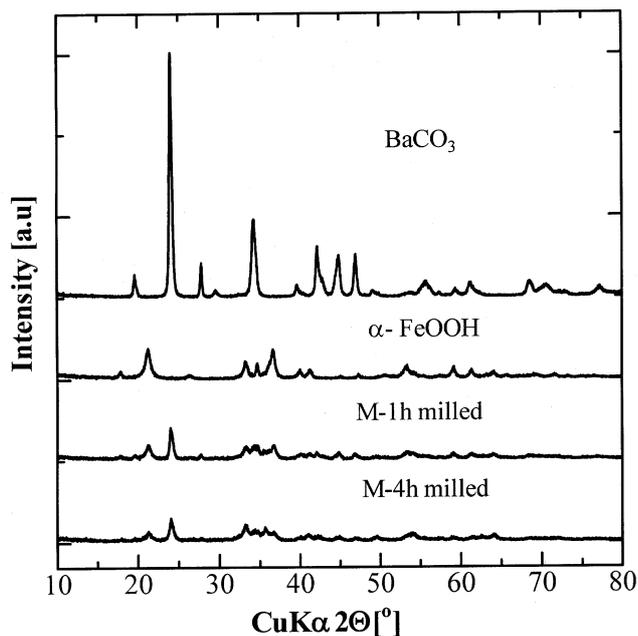


Figure 1. XRD patterns of the raw materials and the mixture (M-) milled for 1 and 4 h.

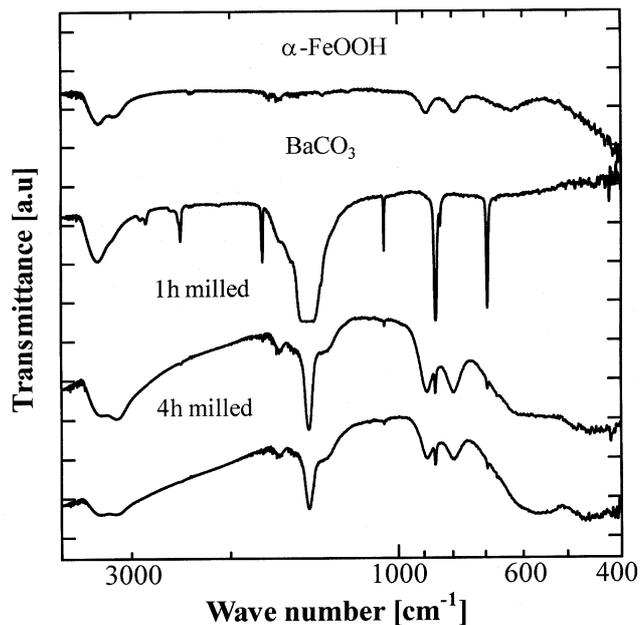


Figure 2. FTIR spectra of the raw materials and the mixture (M-) milled for 1 and 4 h.

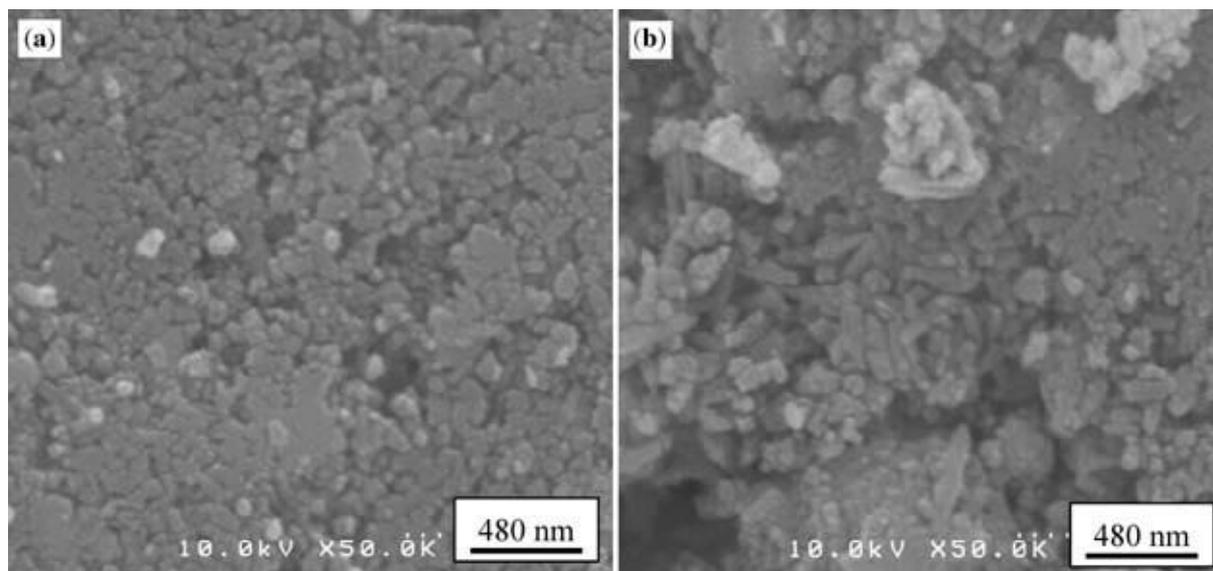


Figure 3. FE-SEM micrographs of the samples milled for 1 h (a) and 4 h (b).

3. Results and discussion

The XRD patterns of the raw materials and samples milled for 1 and 4 h are shown in figure 1. Milling significantly reduced diffraction intensities of barium carbonate and goethite peaks. However, the mixture was not fully amorphized even after 4 h milling. There is a small change in terms of diffraction intensity between the samples milled for 1 and 4 h. Diffraction line broadening of the milled

samples was negligible, indicating its reduction of crystallite size and accumulation of microstrain to be insignificant. Structural changes caused by milling were also examined by FT-IR spectra. As shown in figure 2, barium carbonate is severely affected by milling, as evidenced by the disappearance or reduction of the absorption band intensities at 1450, 1059 and 856 cm^{-1} , being characteristic of the carbonate groups in BaCO_3 . Goethite sample shows absorption bands at 3195, 890, 796 and 3440 cm^{-1} ,

due to OH and H₂O vibrations and a band at 630 cm⁻¹ due to lattice vibration of FeO₆ octahedra as reported previously (Temuujin *et al* 2004). Most of these bands are present in the milled samples. However, a stretching vibration of the raw goethite, $n(\text{FeO}_6)$, appearing at 630 cm⁻¹ became flat by milling for 1 h and broader and centred at 565 cm⁻¹ after milling for 4 h. Similar changes also occurred in the milled Y-phase hexaferrite composition and we have attributed it to substitution of Co cations into octahedral lattice of goethite or partial decomposition of goethite into hematite like structure (Temuujin *et al* 2004). However, M-phase hexaferrite does not have Co atoms in its structure. Therefore, the above mentioned change of $n(\text{FeO}_6)$ vibration is probably related with an appearance of the hematite like structure. Weakening of the carbonate bands of the BaCO₃ and appearance of the hematite like structure may also indicate a chemical bond formation between iron and barium constituents with partial decarbonation.

Scanning electron micrographs of the samples milled for 1 and 4 h are shown in figure 3. The sample milled for 1 h comprises spherical particles with their average particle size between 50 and 60 nm, indicating improved homogeneity and particle size reduction of the starting powders. Increasing the milling time causes some agglomeration with change of morphology from spherical to rod like.

Figure 4 shows XRD patterns of the milled samples after calcining at different temperatures. Both samples calcined at 600°C contain BaFe₂O₄ and α -Fe₂O₃ phases. Solid state reaction for the formation of barium hexaferrite from hematite and barium carbonate usually occurs via 2 steps (Schoeps 1979)



The first reaction starts between 600 and 750°C and the second between 720 and 900°C (Schoeps 1979). Completion of the overall reaction takes place at about 1000–1100°C (Schoeps 1979; Steier *et al* 1999). Therefore, we can suggest that mechanical activation drastically improved the rate of solid state reaction to form barium hexaferrite and the first step was completed at below 600°C. In the present case, the overall reaction was completed at 800°C without any other intermediates. Just 1 h milling was sufficient to cause formation of barium hexaferrite at 800°C. An increase

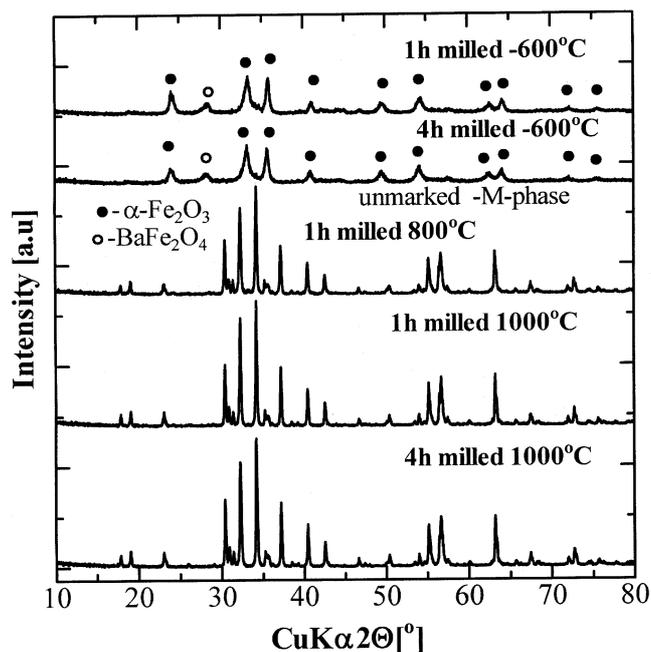


Figure 4. XRD patterns of the milled samples after calcining at different temperatures.

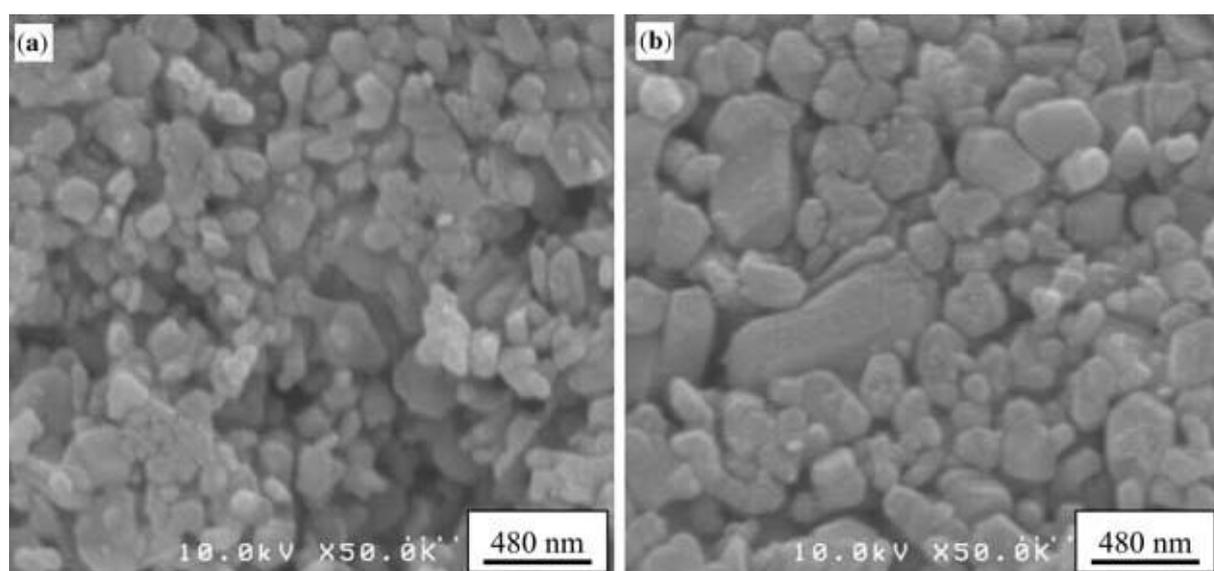


Figure 5. FE-SEM micrographs of the 1 h milled sample after calcining at 800 (a) and 1000°C (b).

in the milling time or calcination temperature does not exhibit any considerable effect on the crystallization behaviour of the *M*-phase. As discussed above, the mechanical activation results in homogenization and possible hetero bridging bond formation between powder constituents during milling and that could be the reason of the improved solid state reactivity.

In the micrograph shown in figure 5 for 1 h milled sample (a), we observe that the barium hexaferrite obtained by calcining at 800°C consists of fine hexagonal particles of about 50–100 nm. By increasing the calcination temperature, sample (b) causes negative consequences, i.e. increasing the average particle size with some abnormal grain growth.

4. Conclusions

Phase pure *M*-phase hexaferrite was synthesized from the mixtures prepared from goethite and barium carbonate by using multi-ring type mill, and subsequently calcining at 800°C. Milling for just 1 h caused similar structural changes with 4 h milled sample. The main reason of the improved solid state reaction rate of the milled mixture is associated with the reduction of the particle size in the starting mixture and simultaneous formation of the hetero bridging bonds toward the products among the dissimilar reaction constituents.

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