JOURNAL OF MATERIALS SCIENCE **37** (2002) 2125–2128

Synthesis of barium hexaferrite by the co-precipitation method using acetate precursor

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Fine particles of barium hexaferrite were synthesised by a chemical co-precipitation method using acetate-nitrate (barium acetate + iron nitrate) precursors. The thermal properties, phase composition and morphology of hexaferrite powders were studied. Simultaneous DTA/TG results confirmed by those obtained from XRD and VSM, indicated that the formation of barium hexaferrite occurs at a relatively low temperature of 710°C. This temperature is affected by the Fe^{3+}/Ba^{2+} molar ratio. The SEM investigations revealed that the mean particle size of barium hexaferrite increases with increasing calcination temperature. In this system the Fe^{3+}/Ba^{2+} molar ratio of 12 (stoichiometric ratio) is favourable. © *2002 Kluwer Academic Publishers*

1. Introduction

Barium hexaferrite, $BaO \cdot 6Fe_2O_3$, due to its relatively large magnetocrystalline anisotropy and good chemical stability has been an established permanent magnetic material since the 1950s [1]. Barium hexaferrite, in the form of ultra-fine particles, is also a suitable candidate for high density magnetic recording applications [2]. Barium hexaferrite is produced mainly by a conventional mixed oxide ceramic method which involves the calcining of iron oxide and barium carbonate mixtures at around 1200°C followed by extended milling to break up the agglomerates [3]. In order to improve the material properties, non conventional routes such as the co-precipitation method [4, 5], salt melt method [6], hydrothermal method [7, 8] and microemulsion method [9] have also been used to synthesise barium hexaferrite. Synthesis of barium hexaferrite from [$FeCl_3 \cdot 6H_2O$-$BaCl_2 \cdot 2H_2O$], ($Fe(NO_3)_3 \cdot 9H_2O$-$BaCl_2 \cdot 2H_2O$] and [αFeOOH-$BaCO_3$] precursors using a co-precipitation method have been reported by numerous investigators [4, 5].

In this paper synthesis of barium hexaferrite from [$Fe(NO_3)_3 \cdot 9H_2O$-$Ba(C_2H_3O_2)_2 \cdot H_2O$] has been investigated. Also, the characteristics of barium hexaferrite produced in this system were compared with those prepared using nitrate [$Fe(NO_3)_3 \cdot 9H_2O$-$Ba(NO_3)_2$] precursor. The characterisation focuses on the morphology, phase composition and thermal behaviour of the products.

2. Experimental procedure

Aqueous solutions of iron nitrate and barium acetate as well as iron and barium nitrates with various Fe^{3+}/Ba^{2+} molar ratios were co-precipitated by the addition of NaOH at room temperature. The molar ratio of $OH^-/(CH_3COO^- + NO_3^-)$ in the acetate-nitrate system and OH^-/NO_3^- in the nitrate system were adjusted to be 2. The co-precipitated products were calcined at various temperatures from 700 to 1150°C for 1 hour in a muffle furnace. A number of calcined samples were pressed at a pressure of 2.8 Tons/cm^2 after mixing with 1% PVA and then sintered at 1250°C for 1 hour in air.

Powder X-ray diffraction (Cu K_α radiation) was used to analyse the phase composition. The thermal behaviour of the co-precipitated samples was studied by simultaneous DTA/TG. The experiments were carried out using 50 mg samples and a heating rate of 10°C/min. Scanning electron microscopy was used to characterise the particle morphology. Magnetic properties of the powder and sintered samples were evaluated using VSM (at the maximum magnetic field of 14 kOe) and permeameter, respectively.

3. Results and discussion

The DTA/TG traces for the sample synthesised in the acetate-nitrate system with a Fe^{3+}/Ba^{2+} molar ratio of 12 are given in Fig. 1. The endothermic peak, at about 100°C, seems to be due to the loss of water from the sample. Four exothermic peaks have also occurred at 300, 650, 710 and 1150°C. The first exothermic peak at 300°C could be due to the conversion of hydroxides to oxides [3]. The exothermic peaks at 650 and 710°C may be attributed to the formation of barium monoferrite ($BaO \cdot Fe_2O_3$) and barium hexaferrite ($BaO \cdot 6Fe_2O_3$), respectively. The last exothermic peak at 1150°C could correspond to the decomposition of barium hexaferrite according to the following reaction as noted by Kojima [1]:

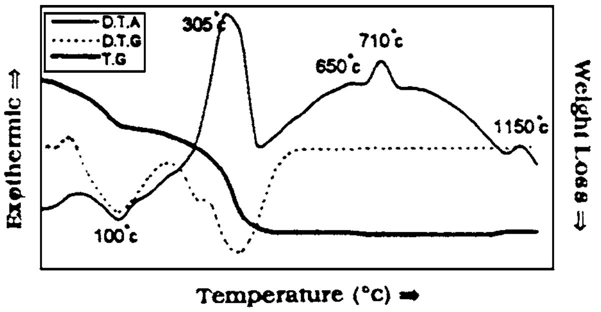

Figure 1 DTA/TG traces of the sample synthesised in the acetate-nitrate system with a Fe^{3+}/Ba^{2+} molar ratio of 12.

$$BaO \cdot 6Fe_2O_3 + BaO \cdot Fe_2O_3 \rightarrow 4Fe_2O_3 + Ba_2Fe_6O_{11}$$

To aid further interpretation of the reaction processes, the DTA analysis was supplemented by XRD analysis. Fig. 2 shows the X-ray powder diffraction pattern for the above sample after it was calcined at 750°C for 1 hour. It appears that the phase composition of the sample mainly consists of barium hexaferrite together with a small amount of non magnetic phases such as barium monoferrite. It is worth mentioning that the formation of barium hexaferrite occurs at a relatively low temperature of 710°C which is in very good agreement with that reported by Jacobo *et al.* [5]. However, higher formation temperatures have been reported by other investigators [1, 10,11].

The intrinsic coercivity and saturation magnetisation of the sample synthesised in the acetatenitrate system with a Fe^{3+}/Ba^{2+} molar ratio of 12 after calcination at 750°C were 52 emu/g and 2.6 kOe, respectively (see Fig. 3). These results also confirm the formation of $BaO \cdot 6Fe_2O_3$ at a relatively low temperature. Existence of some non-ferromagnetic phases such as BaO. Fe_2O_3 is responsible for low value of saturation magnetisation. A bulk sample prepared from the above sample indicated a $(BH)_{max}$ of 1.65 MGOe.

Table I shows the powder X-ray diffraction results for the samples synthesised in the acetatenitrate system with a Fe^{3+}/Ba^{2+} molar ratio of 12 and then calcined at various temperatures for 1 hour. It reveals that the barium hexaferrite is the dominant phase in all of the samples. As the calcination temperature is increased from 900 to 1050°C, there is continued phase transformation from a multi-phase to single-phase system. The presence of some intermediate phases such as αFe_2O_3 in the sample calcined at 1150°C supports the hypothesis of partial decomposition of barium hexaferrite at elevated temperatures [1]. This is also in agreement with the DTA results as illustrated in Fig. 1.

TABLE I Phase composition of the samples prepared in the acetate-nitrate system with a Fe^{3+}/Ba^{2+} molar ratio of 12 as a function of the calcination temperature

Calcination temp (°C)	Phase composition
750	$BaO \cdot 6Fe_2O_3 + BaO \cdot Fe_2O_3$
900	$BaO \cdot 6Fe_2O_3 + BaO \cdot Fe_2O_3$
1050	$BaO \cdot 6Fe_2O_3$
1150	$BaO \cdot 6Fe_2O_3 + \alpha Fe_2O_3$

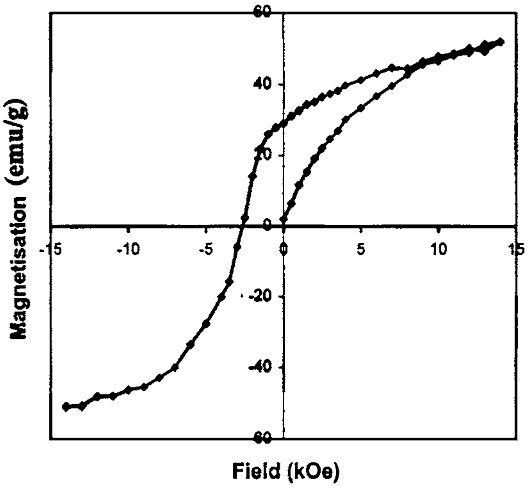

Figure 3 Magnetisation-Field curve of the sample synthesised in the acetate-nitrate system with a Fe^{3+}/Ba^{2+} molar ratio of 12 and then calcined at 750°C for 1 hour.

The DTA/TG traces for the sample synthesised in the same system with a Fe^{3+}/Ba^{2+} molar ratio of 10 are given in Fig. 4. It can be seen that the exothermic peaks have shifted to higher temperatures in comparison with the previous sample. It may be concluded that

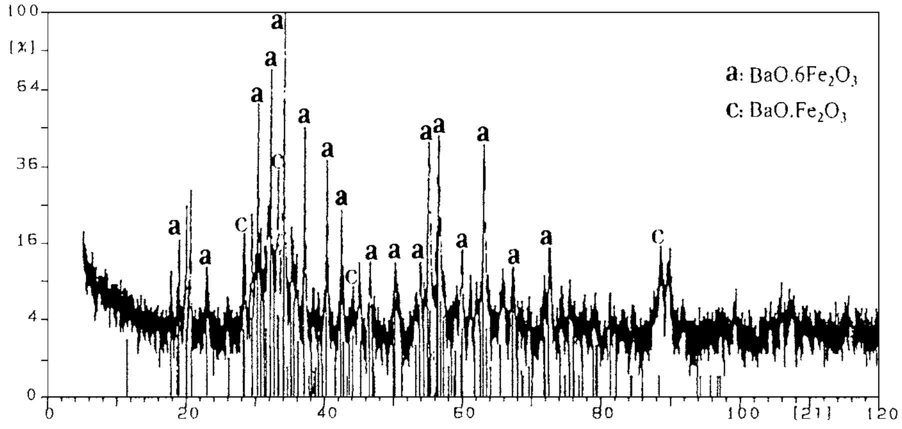

Figure 2 Powder X-ray diffraction pattern of the sample synthesised in the acetate-nitrate system with a Fe^{3+}/Ba^{2+} molar ratio of 12 and then calcined at 750°C for 1 hour.

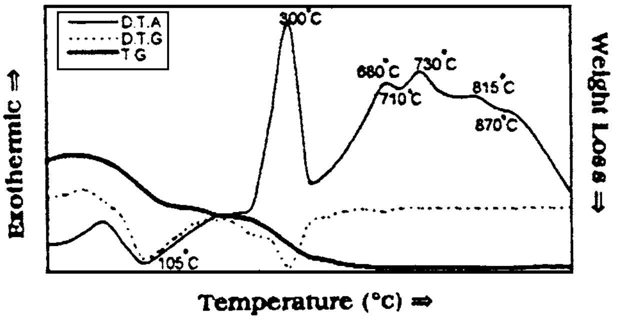

Figure 4 DTA/TG traces of the sample synthesised in the acetate-nitrate system with a Fe^{3+}/Ba^{2+} molar ratio of 10.

the exothermic peak at 730°C is in fact due to the formation of barium hexaferrite and therefore, decreasing the Fe^{3+}/Ba^{2+} molar ratio from 12 to 10 results in an increase in formation temperature of this phase.

Analysis of the XRD pattern of the sample calcined at 750°C for 1 hour confirms the presence of barium hexaferrite peaks together with those for α-Fe_2O_3, Fig. 5. The XRD results of the samples synthesised in the acetate-nitrate system with Fe^{3+}/Ba^{2+} molar ratios of 10 and 12 after calcination at 1050°C for 1 hour confirm that the Fe^{3+}/Ba^{2+} molar ratio of 12 is more convenient for the formation of barium hexaferrite which contradicts the previous results [12]. This may be due to the relatively high pH value of the aqueous solutions produced in the acetate-nitrate system and hence enhanced activity of Ba^{2+} ions.

A typical SEM image of the sample produced with a Fe^{3+}/Ba^{2+} molar ratio of 12 and then calcined at 1050°C for 1 hour, indicating the plate-like particles of the barium hexaferrite with a mean particle diameter of 3 μm, can be seen in Fig. 6. Fig. 7. shows the variation of the mean particle size of the samples synthesised with Fe^{3+}/Ba^{2+} molar ratios of 10 and 12 as a function of the calcination temperature.

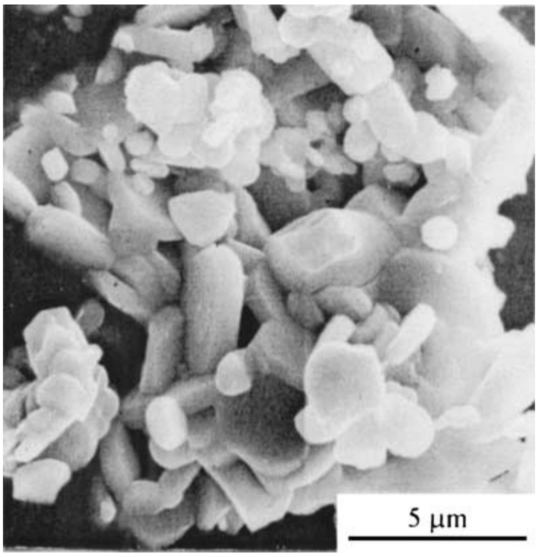

Figure 6 SEM image of the sample produced in the acetate-nitrate systems with a Fe^{3+}/Ba^{2+} molar ratio of 12 and then calcined at 1050°C for 1 hour.

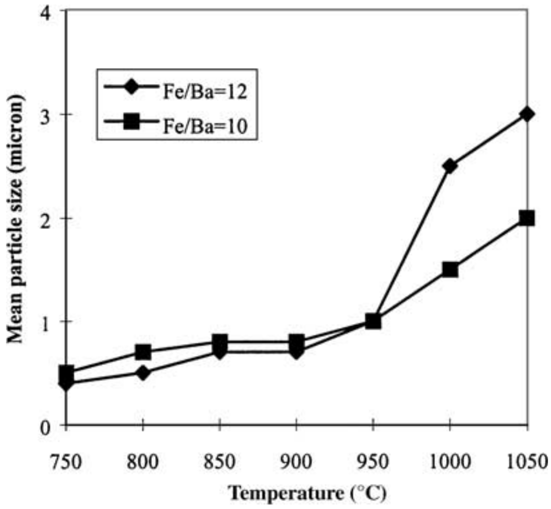

Figure 7 Variation of the mean particle diameter of barium hexaferrite synthesised in the acetate-nitrate system with Fe^{3+}/Ba^{2+} molar ratios of 10 and 12 as a function of the calcination temperature.

The data reveal that the mean particle size in both samples increases with increasing calcination temperature; note the marked inflection in the curves when the calcination temperature exceeds 950°C. While the particle growth behaviour in both samples is similar, the mean particle size of the sample synthesised with a F^{3+}/Ba^{2+} molar ratio of 10 is smaller than that of 12 at elevated temperatures. In fact, the higher growth rate of particles in the sample prepared with a Fe^{3+}/Ba^{2+} molar ratio of 12 seems to be due to the formation of barium hexaferrite in a relatively low temperature.

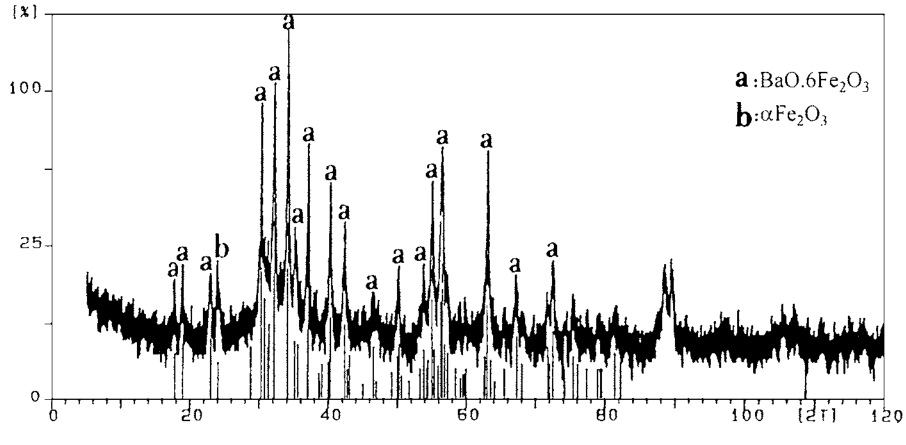

Figure 5 Powder X-ray diffraction pattern of the sample synthesised in the acetate-nitrate system with a Fe^{3+}/Ba^{2+} molar ratio of 10 and then calcined at 750°C for 1 hour.

TABLE II Phase composition of the samples prepared in the nitrate system with Fe^{3+}/Ba^{2+} molar ratios of 8 to 12 and then calcined at 950°C for 1 hour

Fe^{3+}/Ba^{2+} molar ratio	Phase composition
8	$BaO \cdot 6Fe_2O_3 + 2BaO \cdot 3Fe_2O_3 + BaO \cdot Fe_2O_3$
10	$BaO \cdot 6Fe_2O_3 + BaO \cdot Fe_2O_3$
11	$BaO \cdot 6Fe_2O_3$
12	$BaO \cdot 6Fe_2O_3 + 2BaO \cdot 3Fe_2O_3$

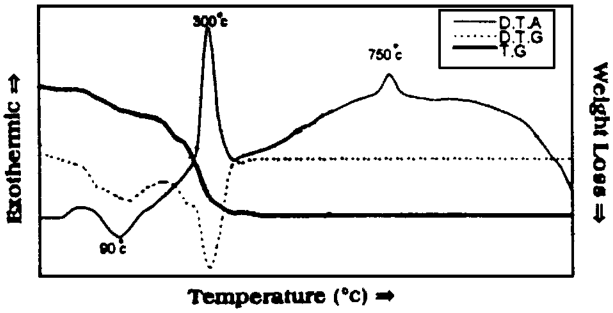

Figure 8 DTA/TG traces of the sample synthesised in the nitrate system with a Fe^{3+}/Ba^{2+} molar ratio of 12.

There is normally an increase in saturation magnetisation with increasing calcination temperature because of an increase in the proportion of the magnetic phase. However, due to the increment of the size of particles above the 950°C, one would expect the coercivity to decrease.

The DTA/TG traces obtained from the sample synthesised in the nitrate system with a Fe^{3+}/Ba^{2+} molar ratio of 12 are shown in Fig. 8. It reveals that the formation of barium hexaferrite in this sample occurs at 750°C which is 40°C higher than that of the acetate-nitrate system.

Analysis of the powder X-ray diffraction patterns of the samples synthesised in the above system with Fe^{3+}/Ba^{2+} molar ratio of 8 to 12 and then calcined at 950°C for 1 hour confirms that the proportion of barium hexaferrite is affected by the Fe^{3+}/Ba^{2+} molar ratio, Table II. The amount of barium hexaferrite increases on increasing the Fe^{3+}/Ba^{2+} molar ratio from 8 to 10 and then exhibits a maximum at 11 which contradicts the results obtained in the acetatenitrate system. It may be concluded that similar to other synthesis routes, in the nitrate system excess Ba^{2+} ions are needed [12].

4. Conclusion

1. In the present investigation, barium hexaferrite was successfully synthesised using acetate-nitrate precursors by the co-precipitation method.

2. The barium hexaferrite can form at a relatively low temperature of 710°C in the acetatenitrate system in comparison with that of the nitrate system.

3. In contrast to other processing systems, in the acetate-nitrate system the Fe^{3+}/Ba^{2+} molar ratio of 12 (stoichiometric ratio) is favourable and excess Ba^{2+} is not needed.

4. In the acetate-nitrate system, the mean particle diameter of barium hexaferrite increases from 0.4 to 3 μm when the calcination temperature increases from 750 to 1050°C. The calcination temperature has almost the same effect in the nitrate system.

Acknowledgements

The financial support of this work by Research Council of University of Tehran is gratefully acknowledged.

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Received 8 August 2000
and accepted 30 January 2002