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Efficiency and purity control in the preparation of pure and/or aluminum-doped barium ferrites by hydrothermal methods using ferrous ions as reactants

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ABSTRACT

The synthesis of hexagonal barium ferrite ($BaFe_{12}O_{19}$) was studied under hydrothermal conditions by a method in which a significant amount of ferrous chloride was introduced alongside ferric chloride among the starting materials. Though all of the Fe^{2+} ions in the starting material were converted to Fe^{3+} ions in the final product, Fe^{2+} was confirmed to participate differently from the Fe^{3+} used in the conventional method in the mechanism of forming barium ferrite. Indeed the efficiency of the synthesis and the quality of the product and the lack of impurities such as Fe_2O_3 and $BaFe_2O_4$ were improved when Fe^{2+} was included. However, the amount of ferrous ions that could be included to obtain the desired product was limited with an optimum ratio of 2:8 for $FeCl_2/FeCl_3$ when only 2 h of reaction time were needed. It was also found that the role of trivalent Fe^{3+} could be successfully replaced by Al^{3+}. Up to 50% of the iron could be replaced by Al^{3+} in the reactants to produce Al-doped products. It was also found that the ratio of Fe^{2+}/M^{3+} could be increased in the presence of Al^{3+} to produce high quality barium ferrite.

1. Introduction

Hexagonal barium ferrite receives much attention in the field of recording material [1] due to its large magneto-crystalline anisotropy, relatively high saturation magnetization, non-toxicity, excellent chemical stability and good corrosion resistivity. The quality of the product is critical for successful technological applications. In particular it is necessary to provide ultrafine particle size, narrow size distribution and chemical homogeneity. The use of milling processes is not desirable as they cause broad particle size distribution and introduce impurities. Therefore it is particularly important to establish the conditions for the synthesis that will provide the particles with the best possible characteristics.

The mechanism [2] of formation of barium ferrite from barium oxide and ferric oxide was proposed to include the following three reactions:

$$BaO+Fe_2O_3=BaFe_2O_4 \quad (1)$$

$$BaO+6Fe_2O_3=BaFe_{12}O_{19} \quad (2)$$

$$BaFe_2O_4+5Fe_2O_3=BaFe_{12}O_{19} \quad (3)$$

Attempts to synthesize barium hexaferrites by sol–gel [3] and co-precipitation [4–6] processes invariably lead to the partial formation of residual intermediates such as α-Fe_2O_3, γ-Fe_2O_3, $BaCO_3$ and $BaFe_2O_4$ and usually necessitate annealing at temperatures above 1000 °C for several hours which is undesirable as this induces agglomeration of the particles. The synthesis of nano-size barium ferrites at lower temperatures utilizing shorter times is therefore desirable to improve energy efficiency and cost-efficient maintenance of the equipment. The synthesis of barium ferrite by a hydrothermal reaction is preferable as it can be carried out at lower temperatures and the problem of aggregation is therefore reduced. An additional advantage of the hydrothermal method is that fewer unwanted intermediates and/or impurities are obtained. The impurities Fe_2O_3 and $BaFe_2O_4$ in the precursor materials were controlled in the condition optimizing process until they are not detected by XRD in this work.

Although barium hexaferrite has been hydrothermally synthesized using $FeCl_3$ as one of the starting materials, the syntheses were usually carried out using a relatively long time [7–13]. For example, successful hydrothermal syntheses have been carried out by Liu et al. [7] for 48 h at 230 °C who also noted that barium ferrite is the only XRD detectable phase at a reaction duration of 25 h. Li et al. [8] employed 10 h with temperatures ranging from 180 to 260 °C. Duong et al. [9] used 12 h at various temperatures between 150 and 200 °C. Yamauchi et al. [10] reduced the reaction

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time to within 1 h by using a microwave-induced hydrothermal method.

The efficiency of producing barium hexaferrite might be further increased if the mechanism of the reaction could be altered. Usually the starting material is Fe^{3+} and α-Fe_2O_3 is easier to form under the reported conditions. But it should be noted that $BaFe_2O_4$ is involved in the formation of barium hexaferrite as shown in Eq. (3). And Fe_3O_4 is a compound similar to $BaFe_2O_4$ in which Ba^{2+} is replaced by Fe^{2+}. Furthermore, Fe_3O_4 possesses the inverse spinel-type structure, and also there are blocks of spinel structures in magneto-plumbite structure of barium ferrite. While α-Fe_2O_3 possesses a rhombohedral structure which is very different from the magneto-plumbite-type structure, the similarity in structures of Fe_3O_4 and barium ferrite would made the conversion of Fe_3O_4 to the product much easier than that of α-Fe_2O_3. Furthermore, α-Fe_2O_3 is more stable than Fe_3O_4 thermodynamically, especially at higher temperatures, so that α-Fe_2O_3 is easier to form and more difficult to convert to barium ferrite. If the reaction conditions were controlled such that Fe_3O_4 could be formed at some stage and the conversion of Fe_3O_4 to α-Fe_2O_3 is suppressed, then the efficiency of producing barium ferrite would be improved. Since Fe_3O_4 could be formed by the hydrothermal method with $FeSO_4 \cdot 7H_2O$ and $FeCl_3$ [14], introducing Fe^{2+} might improve the efficiency of preparing barium ferrite or induce the formation of γ-Fe_2O_3 the structure of which can be taken as the spinel structure oxide and it is less stable than α-Fe_2O_3. It can also be argued that lower temperature processes such as the hydrothermal method are much more likely to involve Fe_3O_4 than the higher temperature processes such as sol–gel and co-precipitation. Following this logic, the present work shows that the necessary temperature and time for synthesis can be reduced and the purity increased significantly by including $FeCl_2$ alongside with $FeCl_3$ among the reactants and that the presence of Fe^{2+} ions shows some unexpected benefits.

In spinel structure only 1/8 of the tetrahedral holes were occupied. In magneto-plumbite there are only $4f_{IV}$ and only $4f_{VI}$ holes in a unit cell and all of them are occupied by Fe^{3+}. These two kinds of holes have opposite spins to Fe^{3+} in other holes. Only half of the 12k holes are occupied by Fe^{3+}. The magnetic properties can be tailored if these Fe^{3+} are selectively substituted. Barium hexaferrites are often doped with metal ions to alter their magnetic properties as will be discussed later in this work. The substituted ions can weaken the super-exchange between the two sub-lattices in the ferrimagnetic barium ferrite structure that causes the moments to align in an anti-parallel fashion. Aluminum-substituted barium hexaferrites synthesized by hydrothermal precipitation and calcination have been reported by Mishra et al. [15]. However, samples calcined at 1200 °C by this method were found to contain significant amounts of α-Fe_2O_3 impurity. Aluminum-doped barium and strontium ferrites prepared via a sol–gel route using citric acid to complex the ions followed by an auto-combustion reaction have been reported by Shirtcliffe et al. [16]. In this present paper, we investigate the preparation of aluminum-doped barium ferrite $BaFe_{12-x}Al_xO_{19}$, x=0–6 by a pure hydrothermal reaction using ferrous and aluminum ions to replace all of the starting ferric ions together with barium chloride and sodium hydroxide, and establish the optimum conditions for the reaction.

2. Experimental

Analytical grade $FeCl_2$, $FeCl_3$, $BaCl_2$, KNO_3, $Al(NO_3)_3$ and NaOH were used as the starting materials. For studying the effects of including ferrous ions, KNO_3 (to 2%) and appropriate amounts of $FeCl_2$, $FeCl_3$, $BaCl_2$ were used with specific $Ba^{2+}/(Fe^{2+}+Fe^{3+})$ and Fe^{2+}/Fe^{3+} ratios while the concentration of the total amount of $Fe^{2+}+Fe^{3+}$ was kept at 1 mol/L. For studying the effects of including aluminum ions, appropriate amounts of $FeCl_2$, $BaCl_2$ and $Al(NO_3)_3$ were used as required for the formula $BaFe_{12-x}Al_xO_{19}$ (x=0–6.0) with a given $Ba^{2+}/(Fe^{2+}+Al^{3+})$ and Fe^{2+}/Al^{3+} ratio while the total amount of $(Fe^{2+}+Al^{3+})$ was kept at a concentration of 1 mol/l. In both studies, the reactants were dissolved in deionized water, and then NaOH was added two times in excess. The resulting suspensions were sealed in an autoclave cell and heated for the required duration and then cooled to room temperature to produce powders which were then washed repeatedly using deionized water until no Cl^- was detectable and then dried at 80 °C in an oven. Purity of the products was monitored by powder X-ray diffractograms with Cu Kα radiation using a Y-500 X-ray powder diffractometer. The magnetic measurements were carried out at room temperature with a vibrating sample magnetometer (VSM-7300, Lakeshore). The maximum applied field of 15 kOe was used to evaluate the magnetic parameters. Environmental scanning electron microscopy/electron dispersive X-ray analysis (ESEM/EDX, FEI/Philips XL-30) was used for estimation of crystallite size and aggregation.

3. Results and discussion

3.1. The effect of varying the $FeCl_2/FeCl_3$ ratio on the preparation of barium ferrite

The first study involved varying the ratio of Fe^{2+}/Fe^{3+} in the reactants from 10:0 to 0:10 while fixing the $Ba^{2+}/Fe^{2+}+Fe^{3+}$ ratio at 1:11.5 and the temperature and reaction time at 250 °C and 25 h. respectively.

The resulting XRD patterns are shown in Fig. 1 and the product can be clearly identified as Fe_3O_4 at Fe^{2+}/Fe^{3+} ratios of 10:0, 8:2 and 5:5, thus showing that the inclusion of 50% or more of Fe^{2+} is undesirable. This result is consistent with previous work [14] where Fe_3O_4 can be prepared from Fe^{2+} and Fe^{3+} at 120 °C by a hydrothermal reaction. However, in the present work barium ferrite was not observed from a ratio of 10:0 although Li et al. [8]

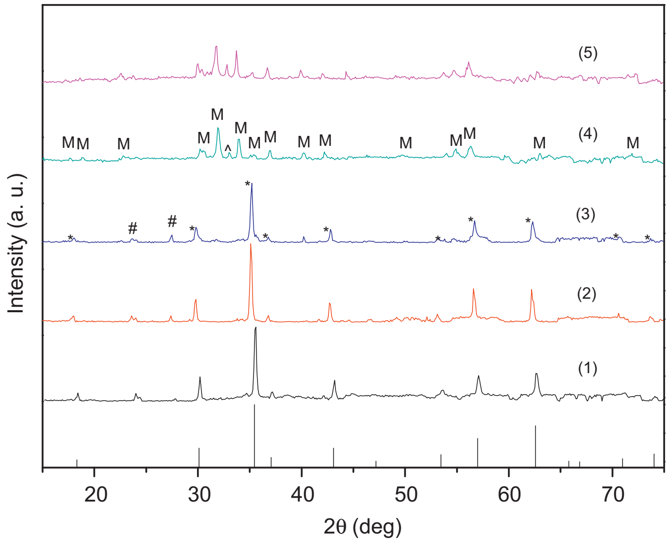

Fig. 1. X-ray powder diffraction patterns of $BaFe_{12}O_{19}$ powders synthesized hydrothermally with different ratios of Fe^{2+}/Fe^{3+}. The $Ba^{2+}/(Fe^{2+}+Fe^{3+})$ ratio was fixed at 1:11.5 and the temperature and time of the reaction at 250 °C and 25 h, respectively. *: Fe_3O_4, #: $BaCO_3$, M: $BaFe_{12}O_{19}$, ^: Fe_2O_3: (1) 10:0, (2) 8:2, (3) 5:5, (4) 2:8, and (5) 0:10. Vertical lines at the bottom: JCPDS65-3107 Fe_3O_4.