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Crystallization of γ-Fe_2O_3 particles with the aid of barium oxide as a catalyst and the effects on magnetic properties

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γ-Fe_2O_3 particles with BaO additives (up to 20 mol%) have been crystallized by solid state reaction of the stoichiometric compositions containing 20 mol% B_2O_3 as a sintering aid. This markedly effects the crystallization and magnetic properties of γ-Fe_2O_3. The microstructure of the samples shows growth of crystallites of considerably smaller sizes and with fairly sharp size distribution after the additions. Crystallites as small as ~ 5 μm size (normally 25 μm) were obtained using 15 to 20 mol% BaO additives in the reaction performed at 1230°C/20 h. This leads to a variation in coercivity over a wide range from 35 to 3500 Oe. Measurements of X-ray diffractometry, magnetization, microstructure and magnetic resonance have been carried out to characterize the magnetic applications of the material. The results are all consistent and elucidate promotion by thermal-treatment of the incorporation of Ba^{2+} into the γ-Fe_2O_3 particle cores.

1. Introduction

It has been observed that the coercivity and other intrinsic magnetic properties [1–4] of γ-Fe_2O_3 can be significantly modified by the incorporation of suitable impurities. Yoshii *et al.* [1] synthesized γ-Fe_2O_3 as thin films showing good uniformity of the material, as required for recording characteristics, by using titanium and copper cation additions. Experiments exploring the addition of BaO and B_2O_3 using the solid reaction process are reported here. It should be noted that the BaO–Fe_2O_3–B_2O_3 composition series, when studied by crystallization from the glass [5–7] gives rise to the crystallization of $BaFe_{12}O_{19}$ ferrite particles. The BaO in the solid state reaction system incorporates ($Ba^{2+} \rightleftharpoons Fe^{3+}$) in γ-Fe_2O_3 and suppresses the crystalline grain growth. B_2O_3, having a much lower melting temperature (~ 460 °C) than the temperatures used for the reaction ($\geqslant 1100$ °C), behaves as a molten flux which facilitates the crystallization of barium-substituted γ-Fe_2O_3 particles. The results are correlated with the development of coercivity and magnetic moments (M_s) in the samples as a function of the thermal treatments for the reaction.

2. Experimental procedure

The barium-substituted γ-Fe_2O_3 particles were prepared by high-temperature solid-state reaction of $BaCO_3$, Fe_2O_3 and B_2O_3 mixed together (compositions are given in Table I) by ball milling in acetone. After drying, the samples were pressed to ribbons of 1 μm thickness (by applying a pressure of ~ 8 ton) and were sintered at temperatures ranging from 1000 to 1400 °C to induce crystallization. The crystals were analysed by X-ray diffractometry and microstructure of the samples.

Magnetization measurements were performed on a PAR Vibrating Sample magnetometer (model 150) with an applied field up to 10 kOe (1 Oe = $1/4\pi \times 10^3$ A m^{-1}). The magnetic resonance spectra of the selected samples were measured with a Varian Associates spectrophotometer (model V-4502-12) in the X-band frequency region. The other experimental details are reported elsewhere [8].

3. Results and discussion

3.1. Crystallization of γ-$(Fe_{1-x}Ba_x)_2O_3$ particles (X-ray diffraction and microstructural aspects)

The γ-$(Fe_{1-x}Ba_x)_2O_3$ particles readily crystallize out in the samples subjected to thermal treatments between 1000 and 1400 °C, showing optimum crystallization yields for treatment at ~ 1230 °C for 20 h. The results obtained for the various samples after a given

TABLE I Compositions investigated with varying amounts of BaO (mol %) in the γ-$(Fe_{1-x}Ba_x)_2O_3$ series

BaO	Fe_2O_3	B_2O_3	Expected value for x	Code
2	78	20	0.01	A
5	75	20	0.03	B
8	72	20	0.05	C
15	65	20	0.10	D
20	60	20	0.14	E

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TABLE II The results of crystallization, particle size and magnetic parameters for the various samples*

Sample	Crystallization yield (wt %)		Particle size (μm)	Magnetic parameters		
	Observed	Calculated		M_s (e.m.u. g^{-1})	H_c (Oe)	M_r/M_s
A	40	90.16	20	24	200	0.10
B	75	90.15	15	30	250	0.12
C	80	90.14	10	33	300	0.18
D	88	90.11	5	40	400	0.20
E	90	90.08	5	41	550	0.31

* All samples were given thermal treatment at 1230 °C/20 h. The particle size data indicate the average particle size. The particles of smaller sizes (up to 0.5 μm) were produced for treatments at lower (~1000 °C) temperatures.

thermal treatment at 1230 °C/20 h are summarized in Table II. Sample E, which contains 20 mol % BaO, gives a maximum crystallization of ~90 wt%. This is very close to the theoretically calculated crystallization of ~90.08 wt %, assuming 100% utilization of the BaO and Fe_2O_3 contents in the crystallization of γ-$(Fe_{1-x}Ba_x)_2O_3$, with $x \leqslant 0.1$. Compositions containing BaO contents higher than 20 mol % were also tried but they did not show useful results. The maximum amount of BaO dissolved in the crystallites appears to be limited to $x \sim 0.1$ (equivalent to 20 mol %).

TABLE III X-ray diffraction lines of γ-Fe_2O_3

d_{hkl} (nm)	I/I_0	$h\,k\,l$	
0.373	5	2 1 0	
0.295	34	2 2 0	
0.278	19	2 2 1	
0.264	–	3 1 0	$a_0 = 0.835$ nm
0.252	100	3 1 1	
0.241	1	2 2 2	
0.232	6	3 2 0	
0.223	0.5	3 2 1	
0.208	24	4 0 0	

Data are taken from JCPDS file 4.755.

The substitution of Ba^{2+} in γ-Fe_2O_3 is evident by the modified X-ray diffraction patterns of γ-Fe_2O_3 [9] shown for the various samples. An example of X-ray diffraction patterns for sample E (sintered at 1230 °C/20 h) is given in Fig. 1. The diffraction data for pure synthesized γ-Fe_2O_3 are given in Table III for comparison. The γ-$(Fe_{1-x}Ba_x)_2O_3$ particles essentially crystallize in a cubic crystal structure with lattice constant $a_0 = 0.839$ nm, which is significantly larger than $a_0 = 0.835$ nm for γ-Fe_2O_3, possibly due to the larger size of the Ba^{2+} cations.

Fig. 2 shows micrographs of typical samples containing 5, 8 and 20 mol % BaO. The average particle size of the sample with no BaO added is estimated (from the micrographs) to be 25 μm, and this was reduced to 5 μm after the addition of BaO. The barium oxide in these samples behaves as an internal catalyst, modifying the particle size in the following two ways: (i) it acts as a nucleus of crystallization, and (ii) it condenses or segregates at grain boundaries during the thermal treatments and retains the diffusion necessary for the growth of the crystallites. The compositions containing the larger BaO concentrations (⩾20 mol %) probably form thick films of barium oxide-rich material at the grain boundaries which interfere with the crystallization process [10].

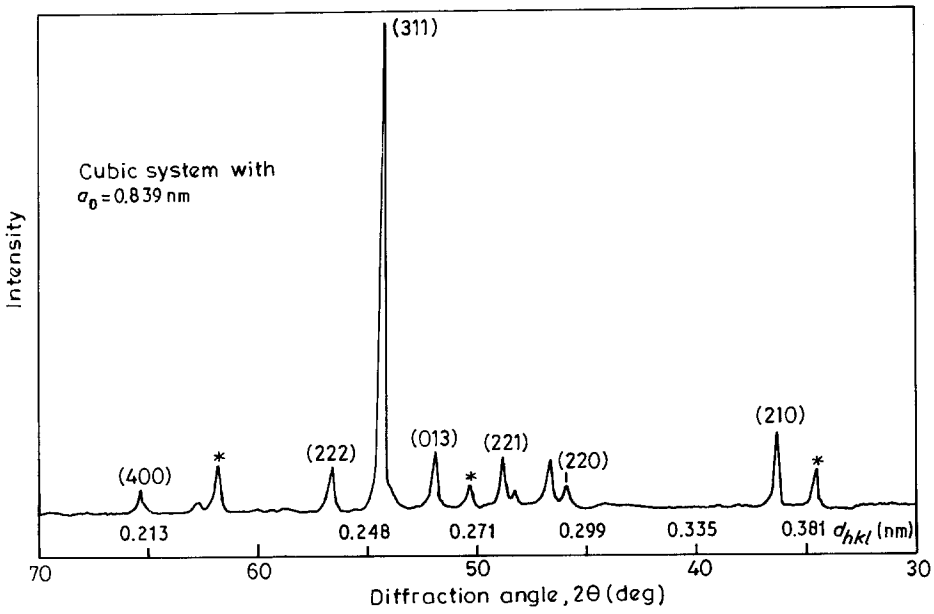
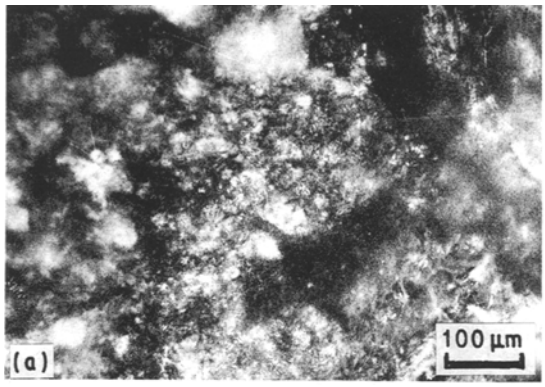
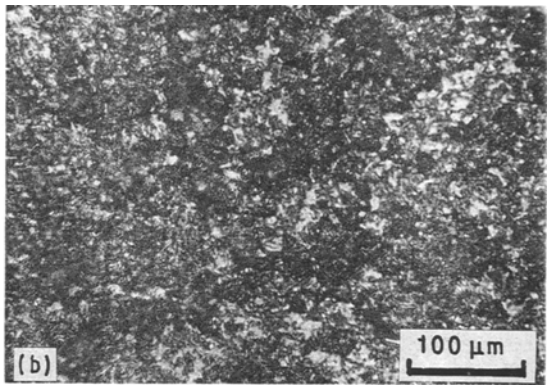


Figure 1 X-ray diffraction patterns for composition series E after the thermal treatment at 1230 °C/20 h. The lines characteristic of the γ-Fe_2O_3 crystalline phase are marked by the ($h\,k\,l$) values. * These lines are not assigned firmly.





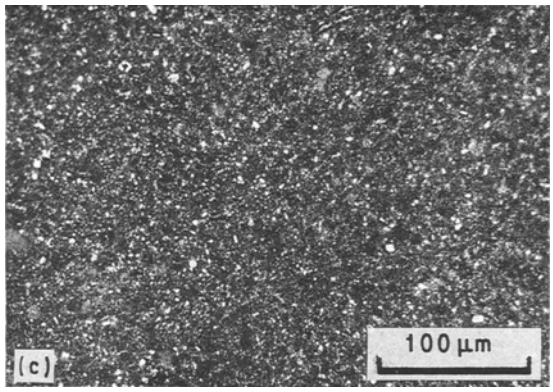


Figure 2 Micrographs showing the effects of BaO addition on the crystalline particle size (white) of γ-Fe_2O_3 crystallizing in the system subjected to thermal treatment (at 1230 °C/20 h). The sample contains (a) 5, (b) 8 and (c) 20 mol % BaO.

3.2. Magnetic properties

Magnetic moments (M_s) of the samples obtained as a function of temperature used for the thermal treatments in the reaction are shown in Fig. 3. The M_s passes through a maximum value for each of the samples corresponding to a treatment at around 1230 °C for 20 h, ensuring the latter to be the optimum condition for the growth of magnetic particles in the present system. The variation of M_s (found to be maximum $\sim$41 e.m.u. g^{-1} for composition series E), however, does not look proportional to the crystallizing mass (see Table II) in the composition series. The crystallites exhibit lower M_s than that expected for γ-Fe_2O_3 magnetic particles. This is likely, if BaO participates in the crystallization, leading to a $Ba^{2+} \rightleftharpoons Fe^{3+}$ type substitution reaction in γ-Fe_2O_3. The Ba^{2+} cations proposed to substitute on the octahedral (Fe^{3+}) sites account for the variation in M_s compared to 65 e.m.u. g^{-1} reported for the pure synthesized γ-Fe_2O_3 [11] observed for these samples. This is consistent with the similar results reported for Co^{2+}-substituted γ-Fe_2O_3 particles [4].

It is interesting that H_c in these samples (Fig. 4) varies from a few Oersted to $\sim$3500 Oe, strengthening the wide field of applications of the product. The samples deduced with characteristically large H_c values ($\sim$3500 Oe) appear important for applications as permanent magnets and those with $H_c \leqslant 10$ Oe for magnetic switching applications [12, 13]. The intermediate H_c values (i.e. of the order of 800 Oe) obtained especially by the thermal treatments at $\sim$1200 °C/20 h of composition series E, look suitable (except that the particle size of the sample is still larger) for magnetic recording applications. The squareness ratio (M_r/M_s) in these samples is found to be $\sim$0.4. More appropriate M_r/M_s values ($\geqslant$ 0.4) for the high-density recording media [1] are achieved corresponding to thermal treatments given at temperatures much below 1200 °C, but they comprise smaller M_s values.

The increase in coercivity for barium-modified γ-Fe_2O_3 particles, compared to that for pure γ-Fe_2O_3

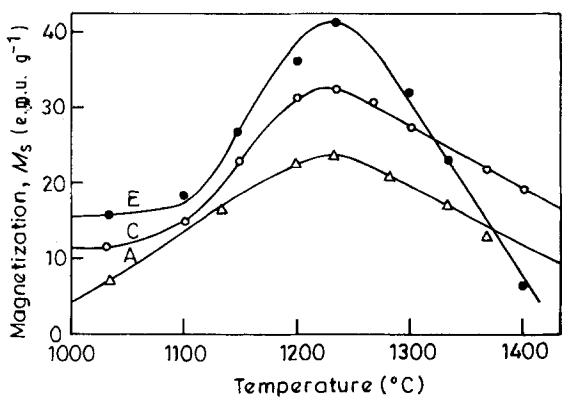


Figure 3 Maximum magnetization (M_s) observed as a function of the thermal treatment of samples in the different composition series. All the samples were exposed for 20 h.

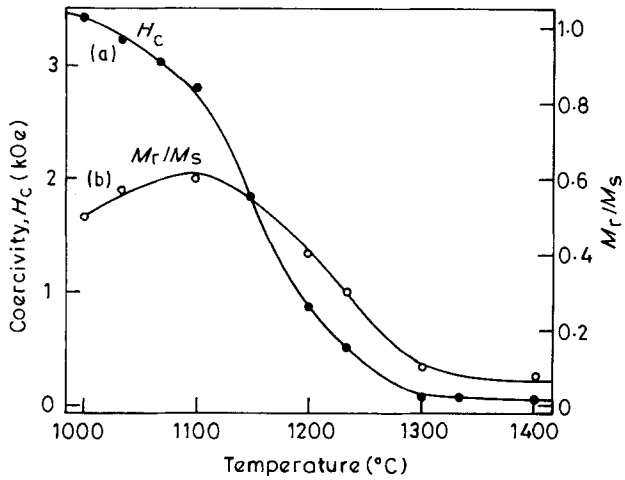


Figure 4 Variation of (a) coercivity and (b) remanent magnetization (M_r/M_s) with thermal treatment for the sample series E.

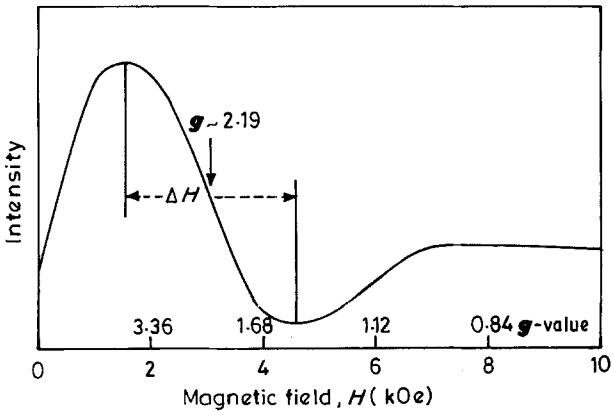


Figure 5 A typical EPR spectrum of composition series E (after treatment at 1230 °C/20 h).

phase ($H_c \sim 130$ Oe) [11], is believed to arise due to diffusion of Ba^{2+} cations into the particle core. This is very similar to the results of Takuoka *et al.* [14] for cobalt-adsorbed γ-Fe_2O_3 particles by thermal treatment. The data of our X-ray diffraction and magnetization measurements are consistent with the hypothesis that thermal treatment results in (apart from the crystallization of the system) barium-diffusion into the γ-Fe_2O_3 particles crystallizing in the system. The latter influences coercivity mainly by modifying the magnetocrystalline anisotropy, H_a ($H_a = 2K_1/M_s$, K_1 being the uniaxial anisotropy constant) following the coercivity relation [15]

$$H_c = p(H_a - H_b) \quad (1)$$

where p is a geometrical parameter and H_b the shape anisotropy factor. This occurs due to the replacement of Fe^{2+} ions in octahedral sites or occupation of Fe^{3+} vacancies by Ba^{2+} ions [12]. A theoretical explanation for this change of H_a anisotropy could be offered by a "one-ion" model [16] involving spin-orbit coupling of the Ba^{2+} ions placed in the trigonally symmetric field of the iron oxide. The thermal treatment of the samples at high temperatures ($\geqslant 1200$ °C) causes the nucleation centres of Ba^{2+} to become thermally randomized among different sites, each with different orientation of the trigonal axis, thus decreasing the uniaxial anisotropy and finally H_c.

3.3. Magnetic resonance

Electron paramagnetic resonance spectra of the various samples exhibit a strong resonance at $g \sim 2.2$ (a typical example is given in Fig. 5), characteristic of the ferrimagnetic resonance of Fe^{3+} ions [7, 15]. The linewidth (ΔH) varies over the range 3 to 2 kOe, with smaller values noticed for the samples given thermal treatment corresponding to the higher temperatures. Several factors, such as porosity, magnetocrystalline anisotropy (H_a), shape anisotropy (H_b) and anisotropy due to growth defects, usually contribute to ΔH in the polycrystalline ceramic materials. A previous investigation [15] studied the individual effects of these factors in some detail for the crystallization of Ca⁻ ferrite as the magnetic particles. The trend observed for ΔH in the present investigation thus indicates a lack of porosity anisotropy factors and development of the contribution from the growth defects, mainly due to multidomain nucleation formation [17] in the system for the thermal treatments at high temperatures.

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