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Barium ferrite: preparation by liquid mix technique and its characterization

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Barium ferrite has been prepared by a novel non-conventional preparation method known as the "liquid mix" technique which involves the preparation of citrates of the metals concerned. The decomposition of the citrates indicated a gradual transition from an amorphous material to a crystalline phase leading to the formation of barium ferrite at 600° C as indicated by the X-ray diffraction and Mössbauer measurements. Submicrometre-sized particles of the ferrite could be obtained directly on decomposition of the citrates, thus avoiding the milling or grinding operations normally employed to reduce the particles to the size required for obtaining good magnetic properties. The best properties (coercivity and remanence) were obtained for the ferrite sintered around 990° C.

1. Introduction

The usual method of preparing barium ferrite ($BaFe_{12}O_{19}$) a permanent magnetic material, consists of firing appropriate mixtures of iron oxide and barium carbonate at a high temperature. The magnetic properties of the ferrite such as coercivity and remanence are found to depend largely on the microstructure of these materials. The coercive force is found to vary with the particle size and is predominantly related to the domain rotation which becomes significant as the crystals approach the size (0.5 μm) necessary to maintain a single domain character. The microstructure of the ceramic is found to depend on many preparative parameters such as grinding, calcining, sintering, density and compaction. In the present work, a relatively new and novel, non-conventional preparation method known as the liquid mix technique [1, 2] has been used in the preparation of barium ferrite. The main advantage of this technique is that the ions are mixed on an atomic scale in the liquid state itself and hence it is possible to accurately control the composition of the product in the initial stages of preparation.

This technique involves the preparation of citrates of the metals concerned and mixing them in solution. These citrates are glass-like in appearance and require further calcination to burn off all the organic material and chemically combine the oxides. The thermal decomposition of the citrates resulted in the formation of barium ferrite at 600° C [3]. Haneda *et al.* [4] have used the non-conventional coprecipitation method for the preparation of barium ferrite at 925° C. They obtained an intrinsic coercivity of 6000 Oe for randomly oriented ferrite samples and 4000 Oe for the sintered samples. Shirk and Buessem [5] obtained a coercivity value of 5350 Oe for isotropic barium ferrite prepared by crystallization of a glass. The electrolytic coprecipitation [6] method has also been used for the preparation of barium ferrite. In this paper we report X-ray diffraction, scanning electron microscopy, Mössbauer spectroscopic and magnetic studies on barium hexaferrite prepared by the liquid mix technique.

2. Experimental details

2.1. Preparation

Barium hexaferrite was prepared from the citrates of iron and barium citrates. Barium citrate was prepared using $BaCO_3$ (BDH, AR) and citric acid (HPC, LR) whereas commercial iron citrate (Riedel–Dattaen, Seelze–Hannover AG) was used. The iron in the ferric citrate was estimated by titration and the citrate to metal ratio was found to be 1 : 1. Fe(III) citrate and $BaCO_3$ were taken in the ratio 12 : 1. The weighed amount of $BaCO_3$ was added to a concentrated solution of citric acid with constant stirring. Strong effervescence of CO_2 was observed indicating the formation of the barium citrate complex which was colourless. Iron citrate solution prepared in distilled water was added to the barium citrate solution. The mixture was heated to dryness at 40° C on a hot plate. The dried citrate mixture was brown in colour and glassy in appearance. It was heated at different temperatures in the range 300 to 800° C.

For studies on sintered barium ferrite, the glassy citrate mixture was calcined at 600° C for 3 h. Several batches of 1.5 g of the powder obtained after calcination were pressed into pellets at 20 000 psi ($\sim 137.8\,N\,m^{-2}$). These pellets were sintered at various temperatures in the range 800 to 1300° C.

2.2 X-ray diffraction

X-ray diffraction (XRD) patterns of the various samples were recorded at room temperature using nickel-filtered Cu$K\alpha$ radiations on a Philips 1730 diffractometer.

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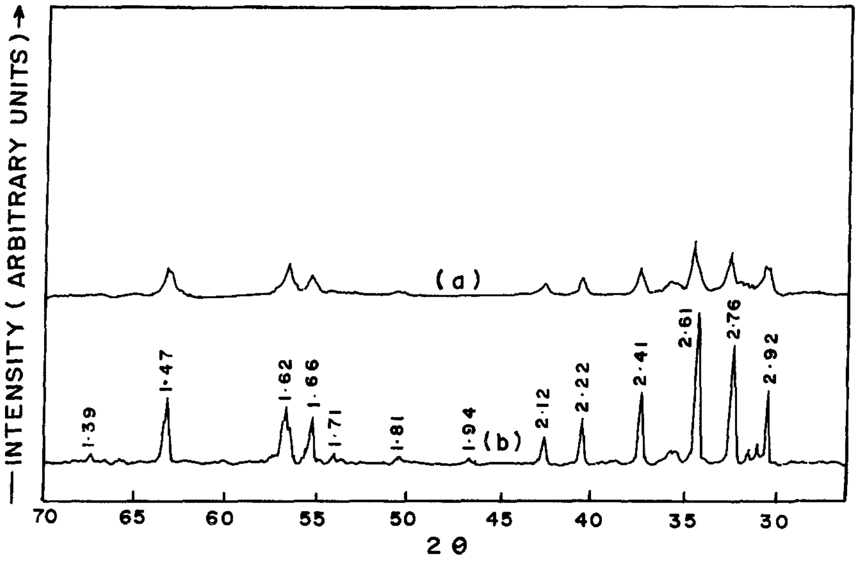


Figure 1 X-ray diffraction pattern of barium ferrite, obtained at (a) 600° C and (b) 800° C.

2.3. Scanning electron microscopy (SEM)

The particle size of the powders calcined at various temperatures were examined using a 150 Cambridge stereoscan scanning electron microscope.

2.4. Mössbauer measurements

The Mössbauer spectra were recorded on a conventional constant acceleration electromechanical drive coupled to ND 100 multichannel analyser operating in time mode. A metallic iron foil (25 μm) was used to calibrate the spectrometer and all the isomer shifts (IS) were measured with respect to metallic iron. The hyperfine (hf) interaction parameters were computed using an iterative least square "MOSFIT" program adopted to ICL 1409S computer.

2.5. Magnetic measurements

The *B–H* hysteresis curves were recorded using a commercial *B–H* recorder (M/s Walker Scientific, Incorporation, USA, model No. MH-1020).

3. Results and discussion

3.1. X-ray diffraction

Examination of the diffraction patterns of the initial citrate mixture and that calcined at various temperatures indicated a gradual transition from an amorphous material to a crystalline phase. The XRD pattern of the powder obtained at 400° C showed the presence of broad lines due to γ-Fe_2O_3 or Fe_3O_4 or both. It was not possible to distinguish between the two oxides as their *d*-values are very close. The XRD pattern at 550° C indicated the appearance of broad lines due to barium ferrite in addition to the iron oxide lines. At 600° C the pattern (Fig. 1a) showed the presence of only the single-phase barium ferrite lines. The observed *d* values [3] are in agreement with previously reported values [4]. The broad diffraction lines indicated the small crystallite size of barium ferrite. The crystallinity increased on calcination at successively higher temperatures. The XRD pattern of the ferrite obtained at 800° C is given in Fig. 1b. The crystallite size of powders obtained on calcination of the citrates at various temperatures is shown in Table I.

TABLE I Crystallite size of powders obtained on calcination of iron citrate + barium citrate mixture at various temperatures

Serial no.	Fe citrate + Ba citrate heating temperature (° C)	Crystallite size (nm)	
1.	400	8	Fe_3O_4
2.	500	9	
3.	600	16	$BaFe_{12}O_{19}$
4.	800	68	

3.2. Microstructure

The microstructure of the ferrite powder obtained at 600° C is shown in Fig. 2. It was observed that the particle size of the powders gradually increased with the calcining temperature but the average particle size of all these temperatures was well below 1 μm. A graph of particle size against temperature is shown in Fig. 3. The photographs also showed that the majority of the particles were more or less uniform in size, homogeneous and spheroidal in shape, but tended to form clusters due to their small size. Thus, submicron sized particles could be directly obtained by the liquid mix technique without employing the grinding or milling operations which are known to introduce lattice strains producing an independent effect on the permanent magnetic properties [8–10]. The microphotographs of barium ferrite sintered at 890, 1200

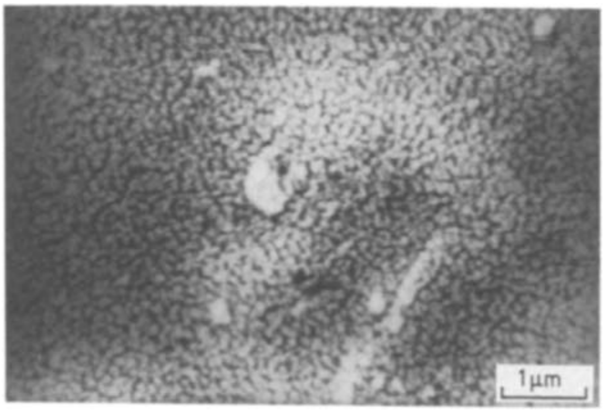


Figure 2 Scanning electron micrograph of barium ferrite powder obtained at 600° C.

TABLE II Mössbauer parameters of iron citrate + barium citrate mixture heated at various temperatures

Temperature (°C)	Type of oxygen environment	Isomer shifts, IS, w.r.t. iron metal ($\pm 0.02\,\text{mm sec}^{-1}$)	Quadrupole splitting, AE ($\pm 0.04\,\text{mm sec}^{-1}$)	Effective magnetic field (± 5 kOe)
As-prepared	–	0.41	0.63	–
250	–	0.30	0.81	–
350	–	0.30	0.81	
400	Complex non-lorentzian spectrum			
550	Complex non-lorentzian spectrum			
600	12k (Oh)	0.39	0.40	416
	4f1 (Td)	0.33	0.11	488
	4f2 (Oh)	0.46	0.23	511
	2b (Trigonal bipyramidal)	0.41	0.99	403
	2a (Oh)	0.50	0.04	511
800	12k (Oh)	0.33	0.22	419
	4f1 (Td)	0.25	0.11	492
	4f2 (Oh)	0.37	0.12	517
	2b (Trigonal bipyramidal)	0.46	1.12	403
	2a (Oh)	0.52	0.00	517

Oh octahedral.
Td tetrahedral.

and 1300° C are shown in Fig. 4. Fig. 5 gives the variation of grain size with the sintering temperature. The average grain size calculated at each temperature is given in Table II. At 1200 to 1300° C all the grains exhibit a perfect plate-like hexagonal structure with the grain boundaries clearly demarcated and there are no pores seen inside the grains.

3.3. Density

The initial step in the sample evaluation is the measurement of sample density. In order to maximize B_r, the remanent induction, it is necessary to approach the single-crystal density which is $5.3\,\text{cm}^{-3}$ [11] for barium ferrite. The density of the pellets sintered at various temperatures were determined from the weight and bulk volume. Fig. 6a gives a plot of the variation of density with the sintering temperature. It is observed that about 78% theoretical density was obtained at a relatively low temperature of 950° C whereas a density of 92% was obtained for the sample sintered at 1200° C. The generally known fact that the density of the material depends on the sintering temperature as well as the grain size has also been corroborated by our observations. From Fig. 3 it is clear that the growth of the grains starts around 1130° C while the rapid rise of density (Fig. 6) has taken place in the temperature range 950 to 1130° C. Thus, for a product of relatively high density but with small grain size as required in the case of high coercivity magnets, the sintering temperature should be above 950° C to obtain maximum density but below 1130° C in order to keep the grain size small. A plot of the ratio (D/d) of density (D) and grain size (d) against the sintering temperature (Fig. 6b) shows that the best sintering temperature would be around 990° C. Table II also shows the expected trend, i.e. increase in B_r with increasing density (increasing sintering temperature), and a fall in coercivity as the grain size grows larger than 0.5 μm and comes into the multidomain region.

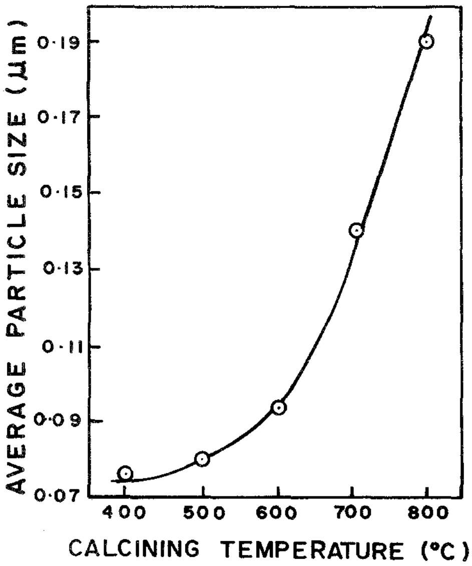


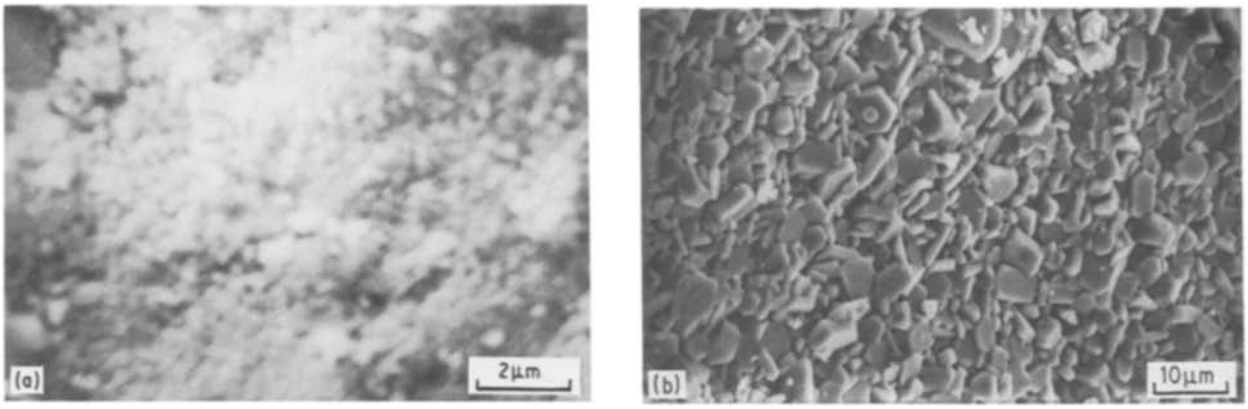
Figure 3 Effect of calcining temperature on particle size.

3.4. Mössbauer studies

The Mössbauer spectra of iron citrate + barium citrate calcined at various temperatures are shown in Fig. 7. The as-prepared citrate mixture is observed to exhibit a doublet (Fig. 7) having isomer shift (IS) and quadrupole splitting (ΔE) values of 0.41 ± 0.02 and 0.04 ± $0.02\,\text{mm sec}^{-1}$, respectively, which agree with the previously reported values for ferric citrate [2]. For the samples heated up to 350° C, the doublet pattern (Fig. 7a to c) is maintained with little change in the Mössbauer parameters (Table III). There is a marked

TABLE III Magnetic properties of barium ferrite, prepared by the liquid mix technique, as a function of sintering temperature

Sintering temperature (°C)	Density (%)	Grain size (μm)	$_BH_C$ (Oe)	B_r (G)	$_IH_C$ (Oe)	$(BH)_{max}$ (kG/kOe)
890	62	0.29	1100	1200	5700	0.36
950	78	0.36	1300	1500	4450	0.55
990	85	0.38	1500	1750	4400	0.64
1050	90	0.50	1600	1800	3750	0.72
1130	91	0.90	1500	1800	3600	0.64
1200	92	5.00	800	1800	1100	0.42



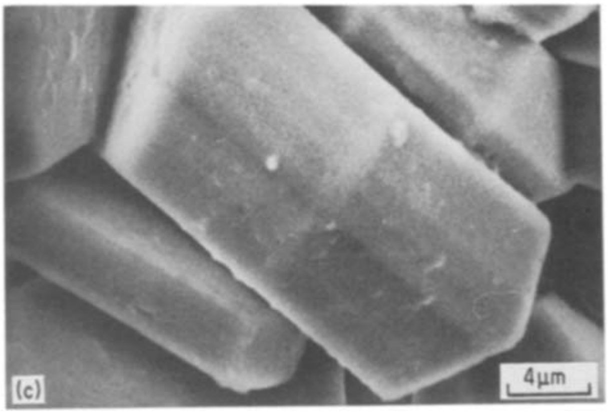


Figure 4 Scanning electron micrographs of barium ferrite sintered at (a) 890° C, (b) 1200° C, (c) 1300° C.

change in the Mössbauer line shape in the temperature range 400 to 550° C (Fig. 7d to e). The spectrum consists of a six-finger pattern with broad resonance lines which could not be resolved unambiguously into subspectra corresponding to either different oxidation states or for ions on different sites in the spinel structure. Similar broadening effects have been observed in many magnetically ordered compounds close to their transition temperature [13]. These complex spectra may be interpreted partly due to the relaxation effects or static distribution of magnetization in the disordered state. It has not been possible to establish the origin of these complex spectra unambiguously. The Mössbauer spectra of the sample heated at 600 and 800° C (Figs 8f, g) correspond to that of barium ferrite. The spectrum at 800° C was almost free from broadening effects thus indicating the formation of well-crystallized barium ferrite. The spectra obtained at these temperatures have been resolved into five different magnetic spectra due to iron located in five magnetic surroundings: (i) 12 K (octahedral), (ii) $4f_1$ (octahedral), (iii) $4f_2$ (tetrahedral), (iv) 2b (trigonal bipyramidal), (v) 2a (octahedral) [14]. The calculated hyperfine interaction parameters are given in Table II. These values are in good agreement with previously reported values [15].

3.5. Magnetic measurements on sintered ferrite

The variation of coercivity, $_BH_C$ with the sintering temperature and the corresponding grain size of the ferrite samples is shown in Table II. The samples heated around 990 to 1050° C exhibit higher $_BH_C$ values thus indicating that at these temperatures the particles appear to assume an increasingly single-domain character. The higher values also result from the orientation of the defect-free single-domain particles obtainable by the liquid mix technique. Orientation may also occur during sintering of the fine particles and during the process of pelleting.

It is observed from the table that at 990 and 1050° C coercivity values of 1500 and 1600 Oe are obtained, respectively. Above 1050° C the samples exhibited a decrease in the value of the coercive force. Undoubtedly

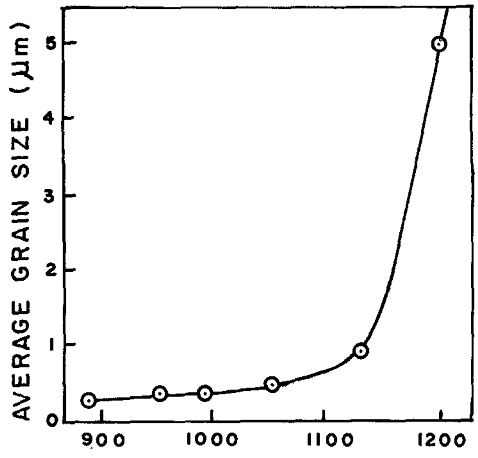


Figure 5 Effect of sintering temperature on grain size of barium ferrite.

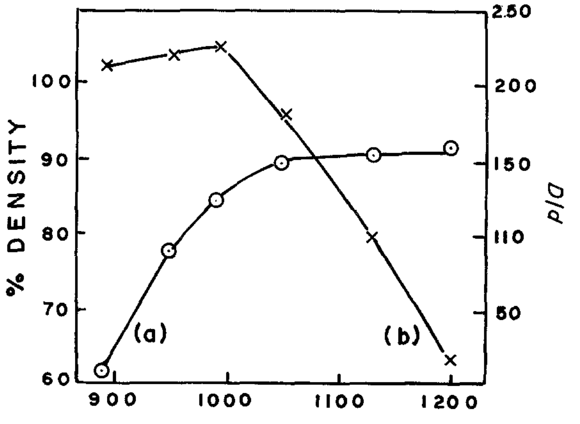


Figure 6 Effect of sintering temperature on (a) density (*D*), (b) ratio of density to grain size (*D*/*d*) of barium ferrite.

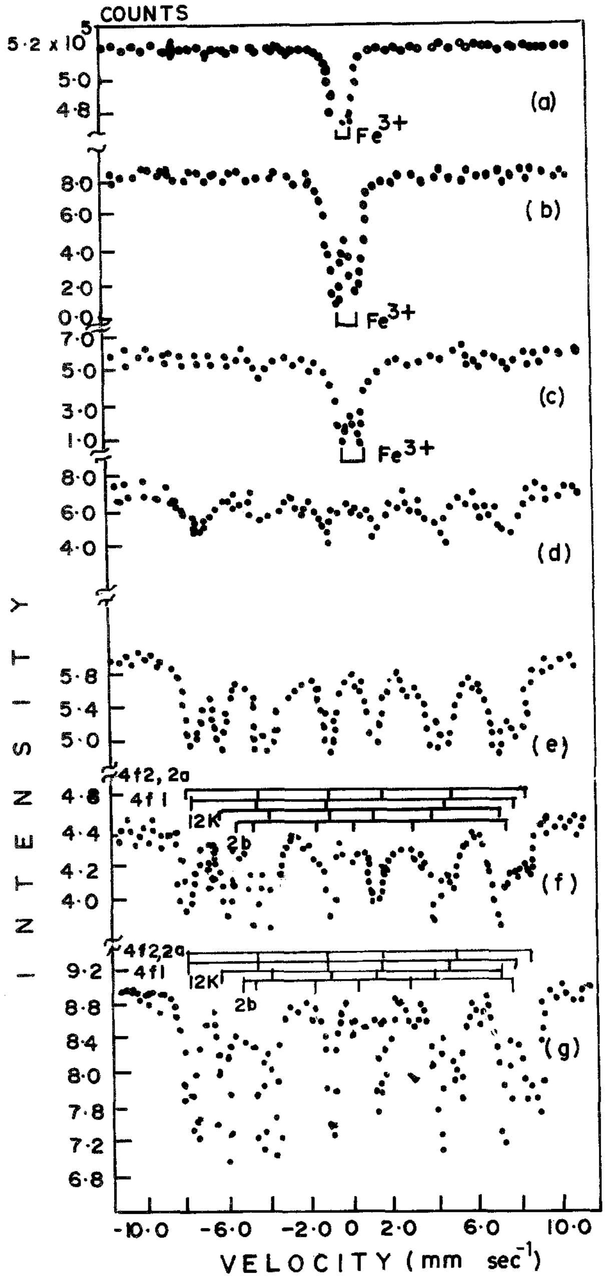


Figure 7 Room temperature Mössbauer spectra of iron cirtrate + barium citrate mixture: (a) unheated, and calcined at (b) 250° C, (c) 350° C, (d) 400° C, (e) 550° C, (f) 600° C, (g) 800° C.

the particle distributions are beginning to shift into the multidomain region. At 1200° C the least coercivity is exhibited. This may be due to the reversal of the intrinsic induction due to movement of the boundary between two magnetic domains. The variation of remanence, B_r, with grain size and the sintering temperature is also given in Table III. It has been found to increase with the size of the grains and the corresponding sintering temperature, attaining a maximum value of 1800 G at 1200° C. B against H and $(B\text{–}H)$ against H curves for the sample sintered at 990° C are shown in Fig. 8. The $(B\text{–}H)$ against H plot shows an intrinsic coercivity (${}_{\mathrm{I}}H_{\mathrm{c}}$) of 4400 Oe. The decrease in ${}_{\mathrm{I}}H_{\mathrm{c}}$ beyond 1050° C can be attributed to particles exceeding the critical domain size due to sintering.

Although the microstructure of the ferrite material results from the time and temperature of sintering, increased temperatures give improved remanence but reduction in the coercive force as the grain size increases. Thus different routes give optimum coercivity or optimum $(BH)_{\mathrm{max}}$ (the maximum value of the product of the magnetic induction and the applied field).

4. Conclusion

As the fine grain size and high density are the key requirements for the formation of good barium ferrite magnets, the above results successfully prove the applicability of the liquid mix technique. The ferrite powder obtained on the decomposition of the citrates can be used for preparing sintered magnets. The properties of these ferrite samples are at least equivalent to those prepared conventionally, but the principal advantage of the method lies in the reproducibility of the product, controlled microstructure, low reaction and sintering temperature and relatively pure materials.

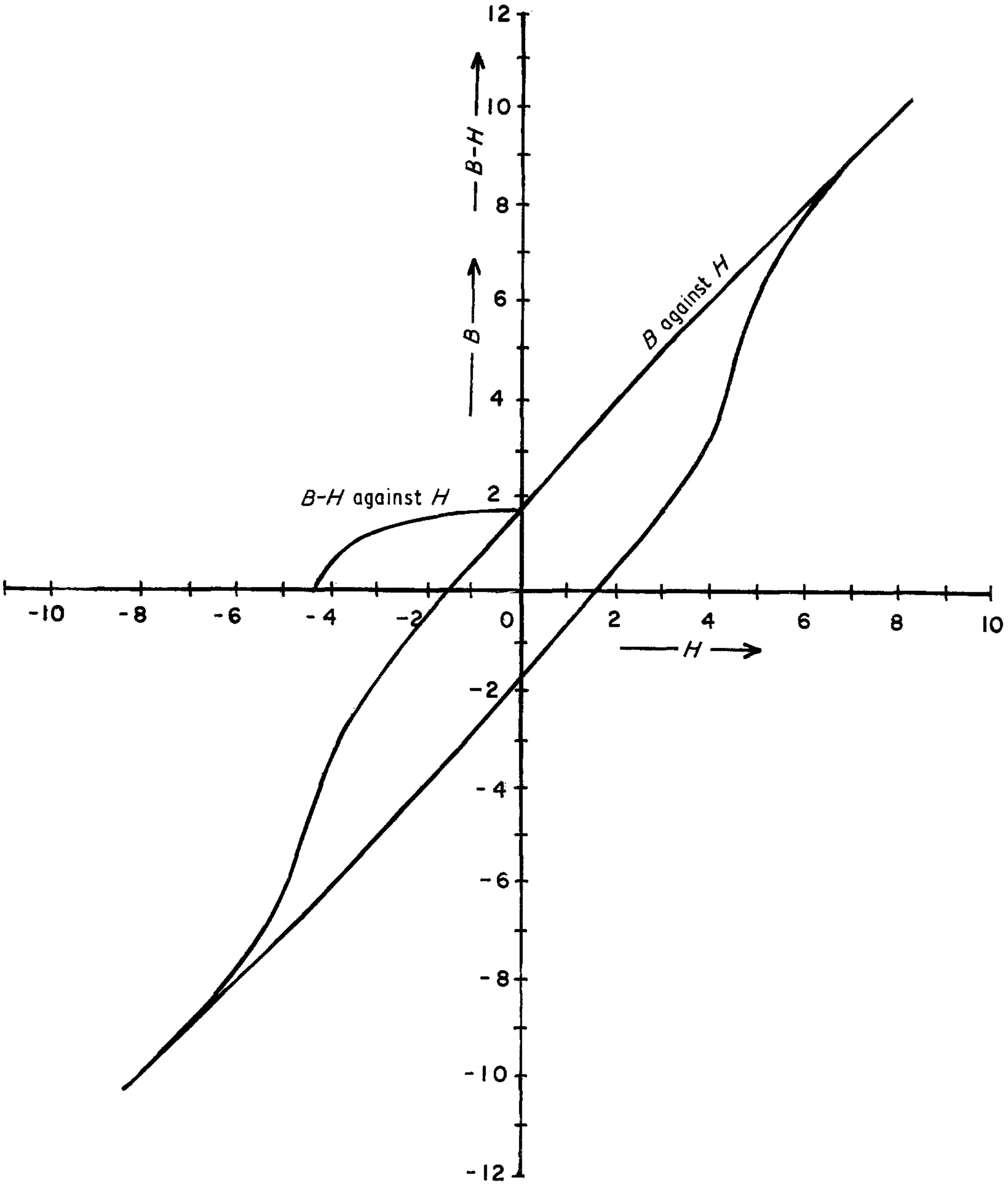


Figure 8 Hysteresis plot of barium ferrite sintered at 990° C.

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