

# The effects of magnetic quenching on glassy barium ferrite

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Barium ferrite ( $\text{BaFe}_{12}\text{O}_{19}$ ) prepared by solution evaporation techniques from ethylene glycol/citric acid or ethylene glycol/pyridine-1-oxide solutions is initially obtained in a glassy form. Although visual observations on samples heated to  $1250^\circ\text{C}$  showed that transparency was maintained in thin sections, X-ray powder diffraction studies showed the development of ordered regions of  $\text{BaFe}_{12}\text{O}_{19}$ . Prolonged heating at  $1250^\circ\text{C}$  resulted in a loss of visual transparency. Samples of partially amorphous material cooled rapidly in a weak magnetic field were found to have a magnetization considerably higher than samples cooled in the absence of a field. Samples rendered polycrystalline by heating for extended periods at  $1250^\circ\text{C}$  showed a lower magnetization on magnetic quenching.

## 1. Introduction

The preparation of mixed-metal oxides of the perovskite type from homogeneous solutions in ethylene glycol has been reported by Pechini [1] and by Eror and Balachandran [2, 3]. A similar technique has been used by Richardson [4] for the preparation of spinel oxides. These methods involve the thermal decomposition of organic complexes of the metals in a liquid phase, and in reported cases the initial product, after removal of organic matter, is a glassy solid. Heating to higher temperatures is required to yield a polycrystalline material. By contrast, Baythoun and Sale [5] obtained lanthanum manganite in an amorphous powder form from an aqueous citric acid gel system. In another study of amorphous oxide systems, Laville and Bernier have studied the crystallization of barium ferrite in a  $\text{BaO} \cdot \text{Fe}_2\text{O}_3 \cdot \text{B}_2\text{O}_3$  glass produced by splat-cooling [6].

Solution evaporation techniques are convenient for the preparation of small quantities of mixed-metal oxides without the extended thermal treatment required by sintering techniques, but there is also an interest in the magnetic properties of glassy and partially crystalline metal oxide phases [6]. X-ray powder diffraction (XRPD) studies have shown that the visually transparent material obtained from solution evaporation and thermal

conditioning between  $700^\circ\text{C}$  and  $1250^\circ\text{C}$  gives diffraction patterns typical of crystalline  $\text{BaFe}_{12}\text{O}_{19}$  with the definition of the diffraction lines increasing with increasing temperature of sample treatment.

It appears from our work that the magnetization of such material, which is considered to consist of small ordered regions of  $\text{BaFe}_{12}\text{O}_{19}$  in a glassy matrix of the same composition, is markedly dependent on whether or not the sample is cooled through its Curie point in a weak magnetic field.

In the preparation of titanates by solution evaporation techniques [1, 3] metal carbonates or nitrates were dissolved in an ethylene glycol/citric acid (EGCA) solvent. The citrate complexes of the metals are formed and then incorporated into a polyester, thermal decomposition of which leads to the metal oxide. Previously, Richardson [4] had used ethylene glycol solutions of pyridine-1-oxide complexes of metal nitrates but in this study barium and iron nitrates were dissolved directly in an ethylene glycol/pyridine-1-oxide (EGPO) solvent system. In this case monomeric pyridine-1-oxide metal nitrate complexes are assumed to be the solute species. The polymeric nature of the EGCA systems provides a viscous liquid medium for the thermal decomposition of the metal complexes and probably helps prevent the separation of particles of solid which might nucleate crystal-

lization. EGPO systems also decompose through a viscous liquid phase whose chemical nature is not presently known.

Both ECGA and EGPO solvent systems have been found to yield equivalent products in the preparation of  $\text{BaFe}_{12}\text{O}_{19}$ . In choosing a solvent system it should be noted that although EGCA solvents are cheaper and citric acid is readily available, the dissolution of metal nitrates is accompanied by the formation of nitric acid.

The dinitrate ester of ethylene glycol is a well-known primary explosive [7] and although no problems appear to have occurred in reported work the risk of its formation should be borne in mind. For this reason it is recommended that work with EGCA solvents and metal nitrates be carried out on the small scale only. Also, citrate systems are well known for forming carbonaceous residues on heating and (where oxygen access is limited) these may cause problems by reducing iron(III) to iron(II) before they are burnt off. Residual carbon has been found to occur in the preparation of perovskites from aqueous citric acid gel systems [5].

## 2. Experimental details

### 2.1. Preparation of metal solutions

Ordinary laboratory grade reagents were used throughout.

(a) EGCA solutions. Appropriate quantities of barium carbonate or barium nitrate and ferric nitrate nonahydrate were accurately weighed out and dissolved by warming in ethylene glycol containing citric acid monohydrate. The weight of citric acid should be about twice that of the metal salts. For example, 0.1086 g of  $\text{BaCO}_3$ , 2.670 g of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and 5.0 g of  $\text{C}_3\text{H}_4(\text{OH})(\text{COOH})_3 \cdot \text{H}_2\text{O}$  were dissolved by warming in 25 cm<sup>3</sup> ethylene glycol. The initial solution was then heated cautiously until a vigorous reaction, accompanied by the evolution of nitric oxides, started. Intermittent heating was continued until no more nitrogen oxides were evolved. The resulting solution was dark brown and showed no visible solid deposition over a period of several weeks. This solution is 0.022 molar with respect to  $\text{BaFe}_{12}\text{O}_{19}$  (2.44 per cent w/v) and has a carbon-to-metal ratio of 22.

(b) EGPO solutions. Appropriate quantities of the metal nitrates were accurately weighed out and dissolved in ethylene glycol along with an approximately equal weight of pyridine-1-oxide. For

example, 0.155 g  $\text{Ba}(\text{NO}_3)_2$ , 2.874 g  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and 2.7 g pyridine-1-oxide were added to 25 cm<sup>3</sup> ethylene glycol. The mixture was heated gently to dissolve the barium nitrate and to remove water. The solution was then heated to the boil and allowed to cool. This solution is 0.024 molar with respect to  $\text{BaFe}_{12}\text{O}_{19}$  (2.63 per cent w/v) and has a carbon-to-metal ratio of 18.

Samples from both solutions were prepared by placing the 6 mm diameter platinum crucible from the thermobalance on a Reichert hot-bench at the 200°C position and injecting 20 μl of the chosen solution into the crucible. This was then gradually moved along the hot-bench to its maximum temperature of about 350°C and left there until no further reaction was evident. This process removes solvent and partially completes the decomposition of the metal complexes. The process was repeated until some 3 to 5 mg of partially decomposed residue was present in the crucible. The crucible was then transferred to the thermobalance for further thermal treatment, which usually consisted of heating samples at 30 K min<sup>-1</sup> to the desired temperature in a stream of air.

Under these conditions EGPO derived samples showed mass stabilization by 400 to 450°C, EGCA derived samples were more variable and usually required heating to 600°C to reach mass stability. Fig. 1 illustrates typical thermogravimetric profiles for samples derived from the two sample systems. It should be noted that if EGPO solutions were not heated to boiling or were prepared using lower proportions of pyridine-1-oxide than quoted above the mass stabilization was delayed. Also, all samples showed a slight continuing mass loss up to about 800°C.

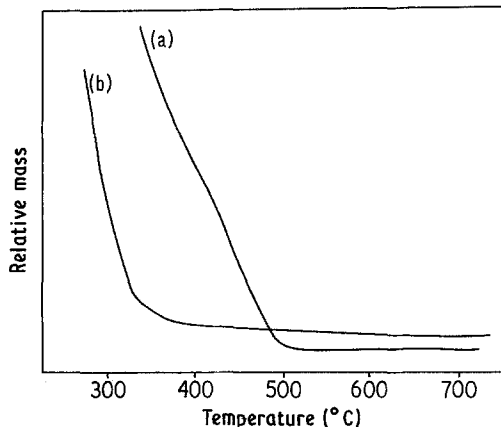


Figure 1 Thermogravimetric profiles of samples derived from (a) EGCA and (b) EGPO solvent systems.

## 2.2. Thermal and magnetic techniques

All thermal conditioning of samples was carried out on a Stanton Redcroft TG 770 thermobalance which is equipped with a small water-cooled furnace of non-magnetic construction with good temperature control. Curie temperature measurements were made by placing a solenoid consisting of about 700 turns of 0.25 mm diameter enamelled copper wire wound on to an aluminium former of 58 mm internal diameter and 24 mm high. This was powered by a power pack producing 0.5 A at 95 V. The field at the sample position, which is central and just above the level of the top of the solenoid, was measured with a Hall effect probe and found to be about  $15 \times 10^{-3}$  T. However, the response of samples inside the furnace indicates that the effective field is about  $5 \times 10^{-3}$  T. Due to the heating effect of the current flow through the solenoid it was only operated intermittently when making observations. The sample temperature was indicated by a platinum-rhodium disc thermocouple situated just below the crucible in the furnace. Apparent changes in weight were observed by connecting the output from the electrobalance bridge to a chart recorder.

The Curie temperature of a sample was taken to be the minimum temperature at which no change in indicated weight occurred on applying current to the solenoid.

Comparative measurements of magnetization were made using a solenoid consisting of about 1000 turns of 0.25 mm diameter enamelled copper wire wound on to a polymethylmethacrylate former of 30 mm internal diameter and 24 mm high. This was situated on top of the furnace with a 7 mm cork spacer. The thermobalance allows the furnace to be lowered away from the sample crucible and, when this is done, the crucible is positioned just below the bottom of the solenoid. This position was found to maximize the change in apparent weight on applying a current to the solenoid. Power was provided by a small power pack, normal operating conditions being to use a current of 0.3 A. This generated a field of  $10 \times 10^{-3}$  T at the sample position as measured by a Hall effect probe.

The magnetization of samples was taken to be proportional to the percentage change in indicated weight on applying the magnetic field. To allow for cases where the decrease in indicated weight exceeded 100 per cent the output from the electrobalance was read on a digital millivoltmeter.

Two methods of measuring the relative magnetization of a sample were used. For "quenched" measurements the solenoid was switched on before lowering the furnace so that the sample was brought rapidly into the magnetic field which was maintained until the sample had cooled to ambient temperature (a microscope slide was placed across the top of the furnace to protect the crucible from convection currents).

The change in the balance output on switching on and off the magnetic field was then noted. The decrease in indicated weight on applying the magnetic field was calculated as a percentage of the indicated weight in the absence of the magnetic field. Three readings were taken in each case. For "normal" measurements the furnace was lowered with no current applied to the solenoid and the sample allowed to cool before applying the magnetic field. Again, three measurements of the percentage decrease in weight on applying the field were taken.

In general, the same sample was subjected to a series of measurements at increasing temperatures, the furnace temperature being maintained during weight measurements and then increased at  $30 \text{ K min}^{-1}$  to the next chosen temperature with the sample in the furnace. When this temperature was reached the temperature programmer motor was switched off and magnetization measurements made immediately. Both "quenched" and "normal" measurements were made at the same temperature, the sample being returned briefly to the furnace between. In "quenched" measurements the important factor is to cool through the region of the Curie temperature in the presence of a magnetic field. Trials with prepared samples of barium ferrite showed that cooling from  $475^\circ \text{C}$  to  $440^\circ \text{C}$  at  $10 \text{ K per minute}$  produced an effect comparable with the uncontrolled rapid cooling from higher temperatures.

It should be emphasized that these techniques, while allowing the variation in magnetization of a particular sample to be followed, do not allow a calculation of intensity of magnetization or allow accurate comparisons between samples. The sample is usually in the form of a discontinuous layer of variable thickness adhering to the interior of the platinum crucible. This non-reproducibility in sample conformation makes sample-to-sample comparison difficult, but measurements on different samples subjected to the same thermal regime were found to agree within plus or minus 10%.

Accurate comparison with commercial ceramic barium ferrite is also difficult, but as powdered commercial material tended to lift out of the crucible in the  $10 \times 10^{-3}$  T field, it is likely that under "normal" conditions the glassy material has a considerably lower magnetization although weight changes exceeding 100% have been observed on samples heated to 900°C and above.

### 2.3. X-ray diffraction

X-ray powder diffraction data were obtained from film exposed in a 360 mm circumference Debye-Scherrer camera using a Phillips PW 1120/90 power supply and a cobalt target. Samples were prepared by rolling lightly-crushed material into needles with "balsa cement" (nitrocellulose). The line measurements from developed films were converted to *d*-spacing values and compared with those recorded in the JCPDS data files [8].

### 2.4. Visual examination

Samples were examined in the crucibles at  $\times 30$  magnification using a Nikon Type 102 binocular microscope and on glass slides at  $\times 125$  and  $\times 500$  magnification on a Vickers M75 binocular microscope equipped for phase contrast.

## 3. Results and discussion

Response to a magnetic field could be detected in both EGCA and EGPO derived 1 Ba: 12 Fe samples during the decomposition of the organic material at temperatures from 250°C onwards. A Curie temperature was observed at 650°C and XRPD examination of samples heated to 650°C gave a small number of relatively faint diffuse lines (Table I). The calculated *d*-spacings did not allow a distinction to be made between  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and

Fe<sub>3</sub>O<sub>4</sub>. Experiments carried out with iron-only samples gave similar magnetic and XRPD behaviour and, as the iron oxide samples became non-magnetic after heating to 700°C, it appears that the magnetic properties are due to the formation of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> regions in an apparently glassy matrix. Barium-iron samples heated to such temperatures show very little differences between "quenched" and "normal" magnetic responses (Fig. 2), presumably because the Curie temperature of the material is not being sufficiently exceeded. Samples heated to temperatures above 700°C do show an increasingly marked difference between "quenched" and "normal" magnetization with increasing sample temperature. Curie temperatures measured on samples which had been heated to 750°C were in the range 550 to 560°C and samples heated to 850°C gave Curie temperatures around 450°C.

The listed value for BaFe<sub>12</sub>O<sub>19</sub> is 450°C [9]. XRPD examination of samples heated to 850°C gave faint lines which could be correlated with those listed for BaFe<sub>12</sub>O<sub>19</sub> (Table II), although in some samples a faint line at 0.250 nm indicated the presence of a low proportion of Fe<sub>2</sub>O<sub>3</sub>. All samples heated above 800°C gave XRPD results indicating BaFe<sub>12</sub>O<sub>19</sub> crystalline regions to be present although visual examination using transmitted light showed them to be translucent. Samples heated at 1250°C for three hours appears polycrystalline and showed a decreased "quenched" magnetization (Fig. 3).

Although the visual appearance of the samples heated for brief periods at temperatures up to 1250°C showed little change, the XRPD results

TABLE I Comparison of observed *d*-spacings in Ba: 12 Fe samples heated to 650°C and listed *d*-spacings for  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub>

Ba: 12 Fe (nm)	$\gamma$ -Fe <sub>2</sub> O <sub>3</sub> * (nm)	Fe <sub>3</sub> O <sub>4</sub> † (nm)
0.291	0.595	0.297
0.249	0.375	0.253
0.205	0.342	0.210
0.159	0.298	0.171
0.146	0.252	0.161
	0.209	0.148
	0.170	0.109
	0.161	

\*JCPDS data file 15-615.

†JCPDS data file 11-614.

TABLE II Comparison of observed *d*-spacings of Ba: 12 Fe samples heated to 850°C and 1250°C, and listed *d*-spacings for BaFe<sub>12</sub>O<sub>19</sub>

850°C (nm)	1250°C (nm)	BaFe <sub>12</sub> O <sub>19</sub> * (nm)
0.290	0.292	0.386
0.275	0.275	0.294
0.259	0.269	0.277
0.239	0.260	0.262
0.221	0.250	0.242
0.211	0.241	0.223
0.165	0.222	0.213
0.161	0.211	0.181
0.146	0.168	0.170
	0.166	0.167
	0.162	0.163
	0.146	0.147
		0.130

\*JCPDS data file 7-276.

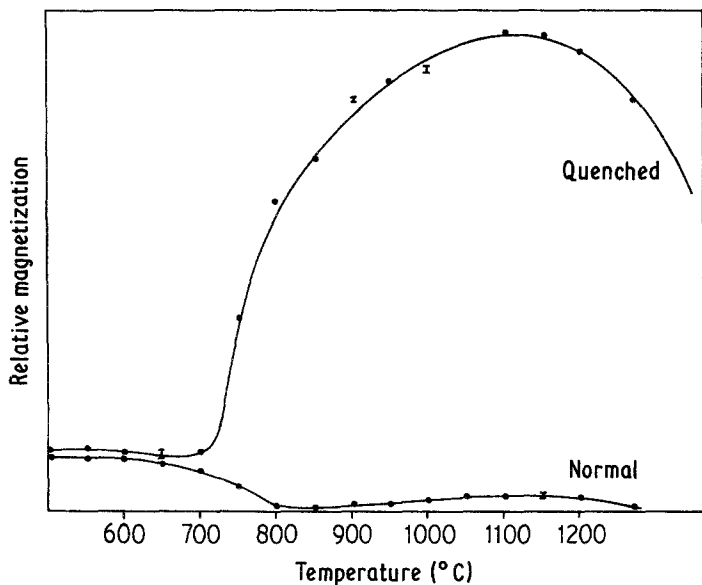


Figure 2 Variation of relative magnetization with temperature for "quenched" and "normal" thermomagnetic treatments.

showed an increasing definition of the diffraction pattern of  $\text{BaFe}_{12}\text{O}_{19}$  and magnetic measurements an increasing difference between "quenched" and "normal" magnetization (Fig. 2). The interpretation of the magnetic results poses difficulties. It appears reasonable to assume that the decrease in "normal" susceptibility from 650 to 850°C is associated with the transition from  $\gamma\text{-Fe}_2\text{O}_3$  to

$\alpha\text{-Fe}_2\text{O}_3$  which is followed by, or accompanied by, the formation of  $\text{BaFe}_{12}\text{O}_{19}$  as indicated by the observed Curie temperatures and XRPD patterns. Samples within this range show a single Curie temperature intermediate between those of  $\gamma\text{-Fe}_2\text{O}_3$  and  $\text{BaFe}_{12}\text{O}_{19}$  which decreased towards that of  $\text{BaFe}_{12}\text{O}_{19}$  with increasing sample temperature.

This is at variance with the results of the thermomagnetic analysis of mixtures of magnetic oxides [10] where the individual Curie temperatures of component oxides were observed.

The results of conditioning Ba: 12Fe samples for extended periods are shown in Fig. 3. Conditioning at 700°C indicates that an equilibrium amount of magnetic  $\text{BaFe}_{12}\text{O}_{19}$  is formed after about one hour. Conditioning at 800 and 900°C shows a slow continuing rise in magnetic response from the initial rapidly attained values whereas conditioning at 1250°C shows a very considerable decrease in "quenched" magnetization over three hours. This was accompanied by a loss of translucency by the sample. XRPD examination showed it still to contain well-defined  $\text{BaFe}_{12}\text{O}_{19}$  with no evidence for any other crystalline phase being present in significant amounts. The Curie temperatures indicated in Fig. 3 were obtained by interrupting the thermal conditioning and again show values intermediate between that of  $\text{BaFe}_{12}\text{O}_{19}$  and those expected for  $\gamma\text{-Fe}_2\text{O}_3$ .

Fig. 2 shows that increasing the maximum temperature to which the samples is subjected increases the "normal" magnetization only slightly but has a marked effect on the "quenched" magnetization

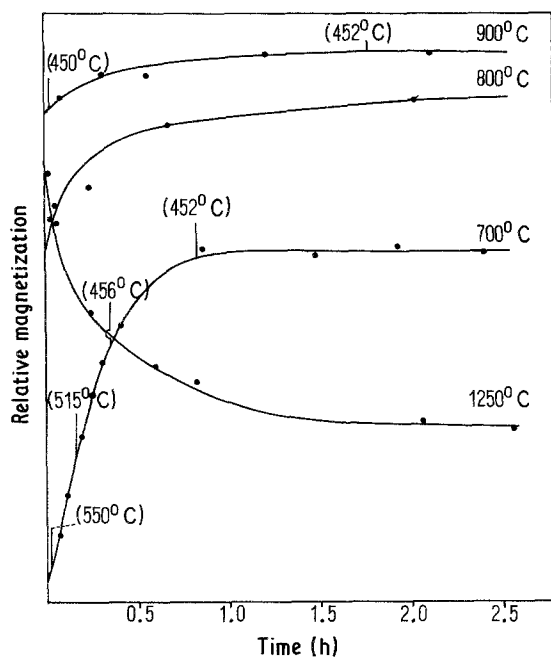


Figure 3 Variation of relative magnetization and  $T_c$  of samples conditioned at various temperatures for up to 2.5 h (figures in brackets are observed Curie points for samples heated to indicated temperature).

TABLE III

Ceramic (nm)	BaFe <sub>12</sub> O <sub>19</sub> * (nm)
0.290	0.289
0.274	0.277
0.258	0.262
0.250	0.252
0.239	0.242
0.221	0.223
0.193	0.194
0.180	0.181
0.168	0.167
0.165	0.163
0.161	0.161
0.146	0.147

\*JCPDS data file 7-276.

which in samples heated to 1250°C typically results in a magnetization some twenty times that observed under "normal" conditions. This enhanced "quenched" magnetization appears to be associated with the generally glassy nature of the material in view of the observed decrease accompanying the conversion to an apparently polycrystalline material.

Samples of BaFe<sub>12</sub>O<sub>19</sub> prepared by ceramic techniques were obtained by crushing commercial magnets. The composition was verified by XRPD (see Table III). The magnetic behaviour of these samples could not be examined using the same magnetic field as previously due to a tendency for particles to lift out of the crucible. Accordingly a reduced field was used when they were examined under "quenched" and "normal" conditions. One sample heated to 600°C showed an approximate doubling of magnetization on quenching and a sample from another source an increase of about five times. These results are roughly in line with those for the solution-derived polycrystalline material.

It thus appears that barium ferrite can be switched between two states of differing magnetization by heating above its Curie temperature and cooling in the presence or absence of a weak magnetic field. This effect is found to be much more pronounced in samples of a generally glassy nature than in polycrystalline samples. Such glassy samples give XRPD patterns showing the presence of ordered regions of BaFe<sub>12</sub>O<sub>19</sub>. The sizes and distribution of these ordered regions remains to be studied but it appears from the visual appearance that the degree of crystallinity is low.

It is well known that slow cooling of magnetic alloys in a weak magnetic field (magnetic anneal-

ing) can give large increases in permeability [11, 12] which are ascribed to induced anisotropy. The mechanism in magnetic oxides is not apparent as yet but it is notable that the enhanced magnetization can be produced by rapid cooling through the Curie point.

This effect appears to be general as it has been found with solution-derived samples of Y<sub>3</sub>Fe<sub>5</sub>O<sub>12</sub>, NiFe<sub>2</sub>O<sub>4</sub> and CoFe<sub>2</sub>O<sub>4</sub> [13]. The behaviour of these glassy oxide samples parallels, in some respects, the behaviour of the BaO · Fe<sub>2</sub>O<sub>3</sub> · B<sub>2</sub>O<sub>3</sub> glasses obtained by Laville and Bernier [6]. They found that crystallization of BaFe<sub>12</sub>O<sub>19</sub> initiated around 670°C and that annealing in a 1.05 T field at 700°C increased the ferrimagnetic properties of their material. They also found their original, non-crystalline, material showed mictomagnetic properties at low temperature.

Such detailed magnetic studies have not yet been carried out on the partially crystalline BaFe<sub>12</sub>O<sub>19</sub> produced in our work, which would appear to consist of small crystalline regions of BaFe<sub>12</sub>O<sub>19</sub> in a BaO · 6Fe<sub>2</sub>O<sub>3</sub> glass, but the pronounced changes in magnetization on quenching in a weak magnetic field indicate that it is worthy of further study.

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