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Barium hexaferrite magnet by topotactic reaction method

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A new topotactic sintering method using αFe_2O_3 (obtained from $\alpha FeO \cdot OH$) and $BaCO_3$ is developed for preparing cheaper grain oriented barium hexaferrite. αFe_2O_3 and $BaCO_3$ (precipitate grade) are wet mixed in a ball mill in stoichiometric proportion. The mixed slurry is then dried at 110° C for about 12 h. The dried powder mixture containing moisture as a binder is uniaxially compacted at 5×10^6–10×10^6 kg m^{-2} pressure. The green compacts are air sintered in the temperature range 1100–1300° C for 1 h. The best results of the sintered ferrite show maximum energy product $(BH)_{max}$ in the range 7–10 kT A m^{-1}. The bulk of commercial requirements for toy magnets etc. may be met by this method of production which eliminates steps like calcination and cost intensive wet magnetic compaction.

1. Introduction

Orientation of grains in materials like barium hexaferrite is necessary for better magnetic properties in ferrite magnets [1]. In the conventional method of production of oriented ferrites, calcined and ground ferrite slurry is wet compacted under a magnetic field and subsequently sintered at high temperature to retain orientation configuration in the sintered product [2]. A relatively simple and inexpensive process for orientating grain structures by unidirectional compaction of anisotropic constituents and subsequent topotactic reaction has been worked out by Tokar *et al.* [3] and Takada *et al.* [4] for a strontium hexaferrite system. Recently Higuchi *et al.* [6] have synthesized lanthanum doped barium hexaferrite from organometallic compounds and Goldman [7] has dealt with the understanding of ferrites in a lucid manner. The present investigation deals with the detailed studies of the preparation of oriented barium hexaferrite by a topotactic chemical (topochemical) method for producing cheaper magnets. This process dispenses with some of the cumbersome process steps by eliminating calcination, grinding and wet magnetic compaction which would result in an effective reduction in the cost of production.

2. Experimental methods

The experimental part broadly consists of two different stages: (1) preparation of sample and (ii) characterization.

2.1. Preparation of sample

2.1.1. Mixing and compaction

αFe_2O_3 obtained from the decomposition of $\alpha FeO \cdot OH$ (goethite) at 400° C was used as one of the starting raw materials (0.1–1 μm particle size) and $BaCO_3$ of AR grade (precipitated, particle size 0.1μm) as another raw material. αFe_2O_3 and $BaCO_3$ were wet mixed in a ball mill for 6–8 h with 1 : 2 solid-to-liquid ratio. The ingredients were mixed in the stoichiometric proportion of 1 : 6 ($BaCO_3$: Fe_2O_3). The mix homogeneity was ascertained by wet chemical analysis. The mixtures prepared showed good homogeneity after 6 h of ball mill mixing. The wet mixture was dried in an oven at 110° C for 12 h. A moisture level of 8–10% was usually maintained in order to facilitate compaction. The homogeneous powder mixture containing moisture as a binder was compacted in a cylindrical die under uniaxial pressure of 5×10^6–10×10^6 kg m^{-2}.

2.1.2. Sintering

The green compacts were slowly dried by gradually raising the temperature to 110° C and keeping the samples at that final temperature for 3 h. The dried samples were then subjected to sintering by heating at a rate of 200° C h^{-1} to different maximum temperatures such as 1100, 1150, 1200, 1250 and 1300° C for 1 h each. They were subsequently cooled at a rate of 200° C h^{-1} until they reached 800° C and thereafter furnace cooled to avoid cracking. The green density and sintered density were determined and the results are shown in Table I and Fig. 4 respectively.

2.2. Characterization

2.2.1. Evaluation of magnetic property

B–H properties of the sintered hard ferrite (barium hexaferrite) were measured in a variable d.c. field magnetizer using induction measuring probes. *B–H* loops of the ferrite sintered at different temperatures are shown in Fig. 2. The hysteresis loops were used to

TABLE I Green density of αFe_2O_3 and $BaCO_3$ mixture under different pressures

Pressure (kg m^{-2})	Green density (kg m^{-3})
5×10^6	1.85×10^3
7.5×10^6	1.9×10^3
10×10^6	2.1×10^3
12.5×10^6	Cracked

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Conventional method

Fe_2O_3 $BaCO_3$

↓

Wet mixing in ballmill

↓

Calcination of mixed powder in the temperature range of 950–1150° C

↓

Wet grinding in ballmill

↓

Wet magnetic compaction

↓

Sintering in air 1100–1300° C

↓

Magnetization of sintered bodies in d.c. electromagnet

Topochemical Method

α-FeO.OH or α-Fe_2O_3 $BaCO_3$

↓

Wet mixing in ballmill for 6–8 h

↓

Directional compaction

5×10^6–$10 \times 10^6\,kg\,m^{-2}$

↓

Topochemical sintering in air 1100–1300° C

↓

Magnetization of sintered ferrites in a d.c. electromagnet

Figure 1 Flow sheets of the production process of hard ferrites by conventional and topochemical methods.

calculate the maximum energy product $(BH)_{max}$ in order to evaluate the permanent magnetic properties.

2.2.2. *Determination of grain orientation*

The X-ray diffraction (XRD) pattern of sintered barium hexaferrite pellets was recorded with a Philips APD-15 diffractometer using a graphite monochromator and Mo$K\alpha$ radiation in order to determine the grain orientation. X-rays were allowed to fall on the flat disc surface of the pellets and the diffracted rays were recorded for 2θ values ranging from 5.5° to 33.2° at a speed of $2°\,min^{-1}$. A number of well defined reflections due to barium hexaferrite was observed.

3. Results and discussion

The flow sheet of the topochemical method *vis-a-vis* the conventional method of ferrite preparation is shown in Fig. 1. As may be seen, expensive process steps like calcination and wet magnetic compaction which are not only energy intensive but cumbersome may be dispensed with in the topochemical method.

The topotactic reaction which involves a solid state chemical reaction gives rise to a product whose crystal orientation is related to the orientation of the initial material. In this work the following reaction takes place

$$\alpha Fe_2O_3\text{ (solid)} + BaCO_3\text{ (solid)}$$

$$\xrightarrow{\text{above }1100°C} Ba0.6Fe_2O_3\text{ (solid)} + CO_2\text{ (gas)}\uparrow$$

αFe_2O_3 and $Ba0.6Fe_2O_3$ have a closely related hexagonal structure, the oxygen and barium ions form close packed lattice. As there is a relationship between αFe_2O_3 and $Ba0.6Fe_2O_3$ structure, the solid state reaction is said to be topotactic.

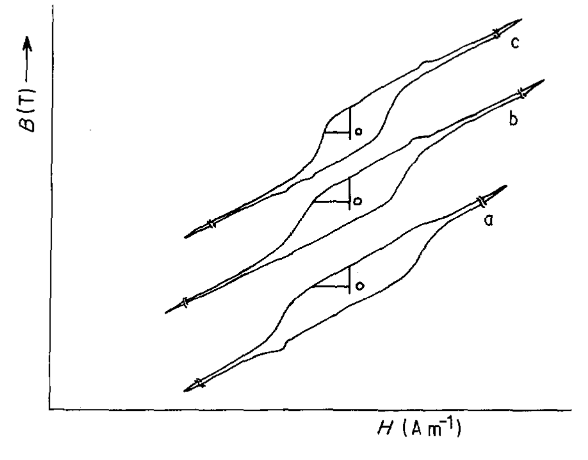

Figure 2 B-H loops of sintered ferrite. a, sintered at 1150° C for 1 h, $(BH)_{max} = 7.557\,kT\,A\,m^{-1}$; b, sintered at 1200° C for 1 h, $(BH)_{max} = 8.456\,kT\,A\,m^{-1}$; c, sintered at 1300° C for 1 h, $(BH)_{max} = 10.063\,kT\,A\,m^{-1}$.

It is evident from the results in Table I that the green density increases with increase in compaction load. Cracks are observed to set in the compacts at a load of $12.5 \times 10^6\,kg\,m^{-2}$. In this work all the samples were compacted at $7.5 \times 10^6\,kg\,m^{-2}$ pressure before sintering. The compacts are found to be hard and crack free after sintering. Sintered density increases with temperature of sintering as depicted in Fig. 4. Densification in the range 1200–1300° C is of high magnitude (30–45%). The enhanced densification may be explained on the basis of the above mentioned chemical reaction where solid state topochemical diffusion of Ba^{2+} and O^{2-} into αFe_2O_3 lattice takes place [4]. Mass transport during the reaction which is responsible for the increased density is brought about by surface and lattice diffusions. Fig. 2 illustrates the hysteresis loops or some of the typical barium hexaferrite compact samples sintered at different temperatures. The product $(BH)_{max}$ represents the ideal operating point for the most efficient use of magnetic materials under static condition. Hence before deciding to make a permanent magnet it is essential to determine first the $(BH)_{max}$ value of any ferrite. $(BH)_{max}$ for the barium hexaferrite samples is observed to be in the range 10–$7\,kT\,A\,m^{-1}$ and the samples sintered at 1300° C for 1 h (Fig. 2c) shows the highest value. These values are within the range of commercial ferrites (2.4–$27\,kT\,A\,m^{-1}$) used in toy magnets, board holders etc. The comparatively higher $(BH)_{max}$ value in the case of 1300° C sintered sample may be attributed to the growth of anisotropic grains at such high sintering temperature. The variation of B_r and H_c with sintering temperature (Fig. 5) shows the decrease of coercive force with increasing sintering temperature. Increase of B_r with sintering temperature is probably associated with formation of ferrite and subsequent growth of these anisotropic ferrite grains perpendicular to the direction of pressing resulting in a near grain oriented structure (confirmed by XRD). A higher coercive force at lower sintering temperature may be explained on the basis of higher porosity at low sintering temperature surrounding the anisotropic grains

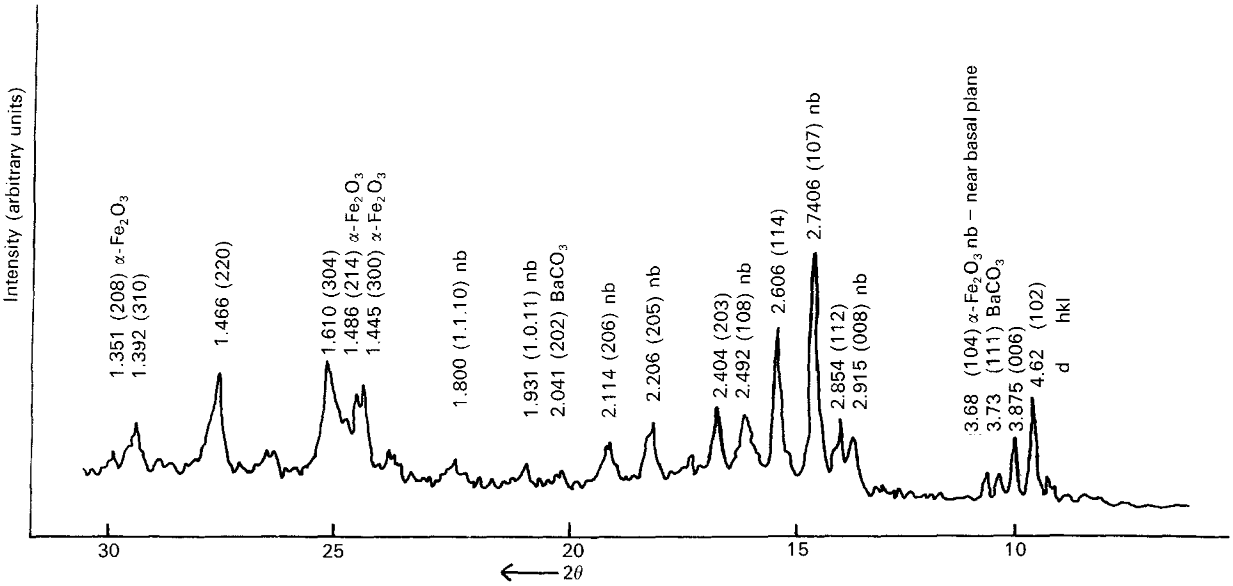

Figure 3 X-ray diffraction patterns of ferrite.

that prevents the rotation of magnetic domains. This is corroborated by the experimental results as shown in Fig. 4.

The XRD patterns of the sintered compacts were taken on the surface perpendicular to the direction of pressing. The diffractogram of a typical compact sintered at 1300° C shown in Fig. 3 exhibits the *d* values of various reflections. Most of the peaks are identified with barium hexaferrite and are comparable with ASTM values (Card No. 7-276). Other peaks which are identified with αFe_2O_3 and $BaCO_3$ may be attributed to the unreacted αFe_2O_3 and $BaCO_3$ present in the sample. If the area under the XRD peak is considered as a measure of the amount of material present, it can then be said that the sintered compacts have grain orientation mostly along the near basal planes like 008, 107, 108, 205 etc. of barium hexaferrite. This is unlike the wet magnetic compaction case where grain orientation is observed to be along the basal plane 001. The presence of some weak reflections due to non-basal planes like 203, 006, 112, etc. are marked, however, their contribution to the grain orientation would be minimal. Besides the above, few reflections of barium hexaferrite due to non-basal planes like 114, 304, 220, 120 are also found to exhibit non-weak intensity.

4. Conclusions

(i) It is possible to prepare crack-free barium hexaferrite ceramic magnets by topotactic reaction method.

(ii) Topotactic reaction/topochemical process overcomes steps like calcination, grinding of calcined powder and wet magnetic compaction. Hence, this process may be suitable for producing low cost ceramic magnets which have good applications in toys, chess board holders, lamp holders, calendar stickers, coin detectors and other holding devices.

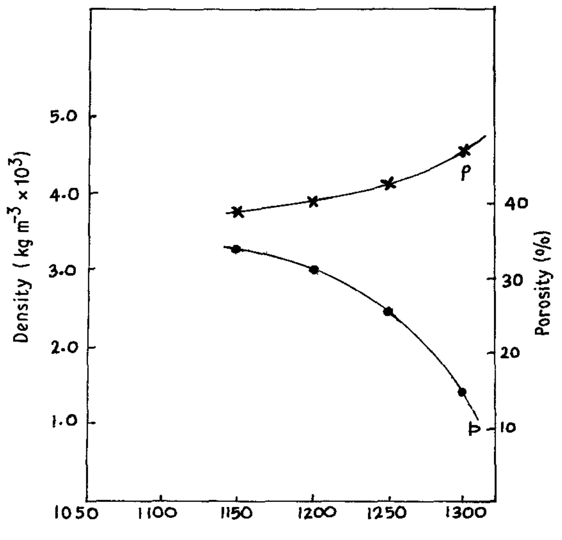

Figure 4 Variation of sintered density (ρ) and porosity (*p*) with sintering temperature.

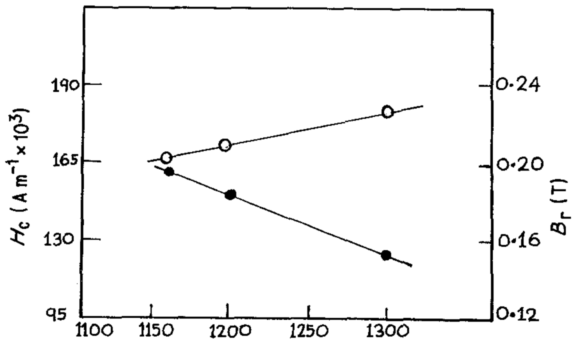

Figure 5 Variation of coercive force H_c (●) and remanence B_r (○) with sintering temperature.

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References

1. M. H. HODGE, W. B. BITLER and R. C. BRADT, *J. Amer. Ceram. Soc.* **56** (1973) 497.
2. F. KLUG and J. REED, *Bull Amer. Ceram. Soc.* **57** (1978) 1109.
3. M. TOKAR, *J. Amer. Ceram. Soc.* **51** (1968) 601.
4. T. TAKADA, Y. HIROSHI, Y. NAGA and Y. BANDO, Ferrites: Proceedings of International Conference, July, 1970, Japan, Koichi Haneda, p. 275.
5. H. KOJIMA, *J. Amer. Ceram. Soc.* **57** (1974) 68.
6. K. HIGUCHI, S. NAUA and S. I. HIRANO, *Adv. Ceram. Mater.* **1** (1986) 104.
7. A. GOLDMAN, *Bull. Amer. Ceram. Soc.* **63** (1984) 582.

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