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A new method for low temperature preparation of barium hexaferrite powders

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The heating behaviour of lyophilized gels composed of ammonium pectate and Ba^{2+} and Fe^{3+} ions was investigated by differential thermal analysis, thermogravimetric analysis and X-ray diffractometry. The formation of barium hexaferrite was found to be complete after 22 h in an oxygen atmosphere at 600° C, whereas in air at 700° C it has been attained after 30 min only. Examination by scanning electron microscopy of the powders fired at temperatures below 800° C showed almost all of the particles to be less than 1 micron in diameter, a condition necessary for the attainment of high coercivity.

1. Introduction

The characteristics of the barium ferrite powders used for manufacturing ceramic or rubber permanent magnets are of great importance because of their influence on the quality of the final product. In particular, to obtain high coercive forces it is necessary that the size of the particles is below 1 micron, so as not to exceed the single-domain size [1]. This result is difficult to reach with industrial manufacturing methods, where the starting materials employed (Fe_2O_3 and $BaCO_3$) require temperatures higher than 1000° C for the reaction to occur at appreciable rates [2].

Diffusion processes are rather fast under such conditions, and result in a multi-domain particle size; a successive milling is therefore needed in order to reduce the particle size from multi-domain to single-domain. Even so, the size conversion is never complete. In addition, the grinding operation introduces lattice strains and defects which lower the coercive force and the saturation magnetization [1, 3, 4]. For these reasons, the magnetic characteristics of commercially available barium ferrites are much lower than would be theoretically expected [5]. To overcome this inconvenience, we decided to investigate other starting materials such as to allow the preparation of the barium ferrites at drastically lower temperatures. This result can be achieved by pre-mixing the salts to obtain homogeneity down to molecular level in the solid state. To accomplish this, we took advantage of the well-known capacity of polyuronates to bind cations on thier molecular chain and to form gels in aqueous solution [6, 7]. Lyophilization of these gels produces a random texture of organic material, in which the ions are dissolved in the solid state.

Barium and Iron (III) nitrates were chosen as starting materials because of their high solubility in water. Pectate was employed owing to its known ability to bind metal cations [6, 8] and to give stable gels in high ionic strength aqueous solution [8]. Moreover, it is a comparatively cheap compound, although other less expensive, gelling products could be indicated. Since iron nitrate does not exhibit a definite stoichiometry, its Fe^{3+} content must be determined each time a new batch is employed.

2. Experimental details

2.1. Gel preparation

In each preparation, 1 g of pectic acid (Sigma Chemical Co., Catalog No. P-3889, sold as polygalacturonic acid) was dissolved in 80 ml of bi-distilled water with the addition of 2 M NH_4OH. The pH of the clear solution was around 6. This solution was added, under continuous stirring, to a solution of 4×10^{-4} moles of $Ba(NO_3)_2$ (C.Erba

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R.P.) in 40 ml of water. The white microgel obtained was added, under stirring, to a solution of 4.8×10^{-3} moles of $Fe(NO_3)_3 \cdot 9H_2O$ (Riedel-De Haen A.G.) in 40 ml of water. The orange gel formed was homogenized with a fast blender, rapidly freezed in a CO_2–acetone bath, and finally lyophilized.

2.2. Measurements

The thermal evolution of lyophilized gels was followed by means of differential thermal analysis (DTA) and thermogravimetric analysis (TG), with a heating rate of 5° C per minute.

X-Ray diffraction patterns were taken with a Guinier–de Wolff camera and a Siemens diffractometer, using Cu$K\alpha$ and Cu$K\alpha_1$ radiations, respectively.

Firings were carried out in an electric tube furnace; the samples were placed on platinum stripes. The chemical composition of the powders resulting from the thermal treatments was determined by means of an atomic absorption spectrometer.

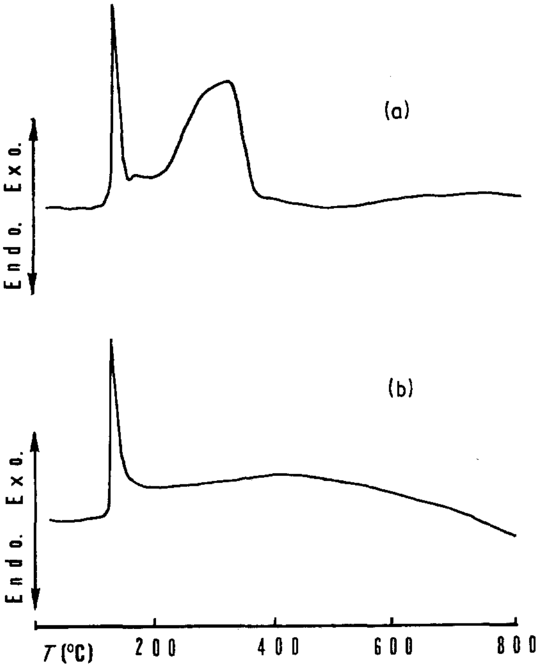

Figure 1 DTA curves for the lyophilized gel (heating rate 5° C min^{-1}): (a) in air; (b) in flowing nitrogen.

3. Results and discussion

When subjected to X-ray diffraction analysis, the freeze dried gels were found to be amorphous. Occasionally, for some of the preparations investigated, weak and broad lines were observed, suggesting the partial presence of the crystalline form of $Ba(NO_3)_2$. Subsequent experiments, however, showed that the behaviour of samples containing small amounts of this crystalline phase was similar to that of the completely amorphous samples.

Differential thermal analysis in air showed two exothermic peaks, at 120 and 330° C. The first peak can be tentatively attributed to the simultaneous presence of oxidizing groups (NO_3) and organic matter, while the second can be due to the combustion of residues of the first reaction. This hypothesis seems to be confirmed by DTA measurement carried out in a nitrogen atmosphere: under these conditions, the first exothermic effect was still observed, whereas the second was not found (Fig. 1). In agreement with the results reported by other authors [9], no thermal effect attributable to the formation of barium hexaferrite could be detected in the temperature range investigated (20 to 1000° C). Since the reaction responsible for the first exothermic peak is rather vigorous and in order to avoid deflagration, the lyophilized gel was decomposed before firing by slow heating up to 200° C under well ventilated conditions.

After this treatment, the material appeared as a black powder, still containing a considerable amount of organic matter, as it can be inferred from the behaviour of the TG curve in air reported in Fig. 2.

The amorphous state is kept up to 500° C even after a long period of heating (12 h). At 600° C, the X-diffraction patterns of samples kept at this temperature for 1 h showed the lines of Fe_3O_4 and of the low-temperature γ-form of $BaFe_2O_4$ [10, 11].

The presence of Fe^{2+} ions is due to the reduction of Fe^{3+} ions by the considerable amount of organic matter present. After 22 h, besides the lines of the two above mentioned compounds, the most intense of the barium hexaferrite lines were also observed. This led one to conclude that, under these conditions, the rate-governing step for the $BaO.6Fe_2O_3$ formation is the oxidation of the Fe^{2+} ions. In fact, the presence of Fe_2O_3 could not be detected by X-ray diffractometry. It seems therefore likely that this compound, immediately after its formation, first reacts with barium oxide to give the monoferrite and further reacts with barium oxide to give the hexaferrite.

To test this hypothesis, we carried out firings in

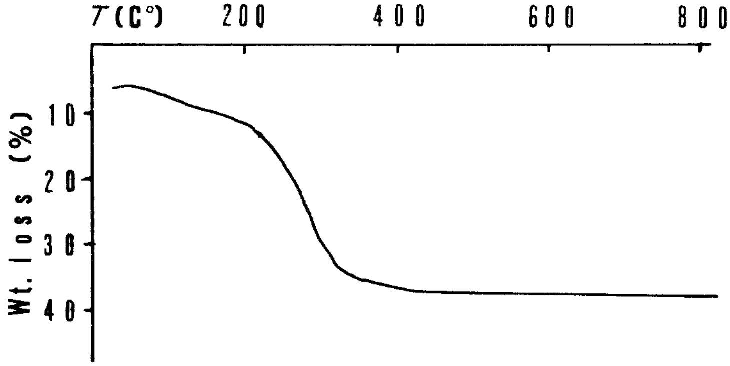

Figure 2 TG curve in air for the lyophilized gel, after prefiring at 200° C.

an oxygen atmosphere so as to accelerate the oxidation process. In fact, under these conditions the formation of $BaO.6Fe_2O_3$ at 600° C was complete after 22 h. At 700° C, after 10 min of firing, both the Fe_2O_3 and the monoferrite were found to be simultaneously present; after 30 min more, the reaction was complete and the X-ray diffraction pattern exhibited the lines of the $BaO.6Fe_2O_3$ alone. Fig. 3 shows the X-ray diffraction patterns of the compound heated as reported above. An attempt to accelerate the reaction by introducing a flow of oxygen into the furnace did not lead to appreciable results. At 800° C the reaction is virtually instantaneous; the samples from DTA tests

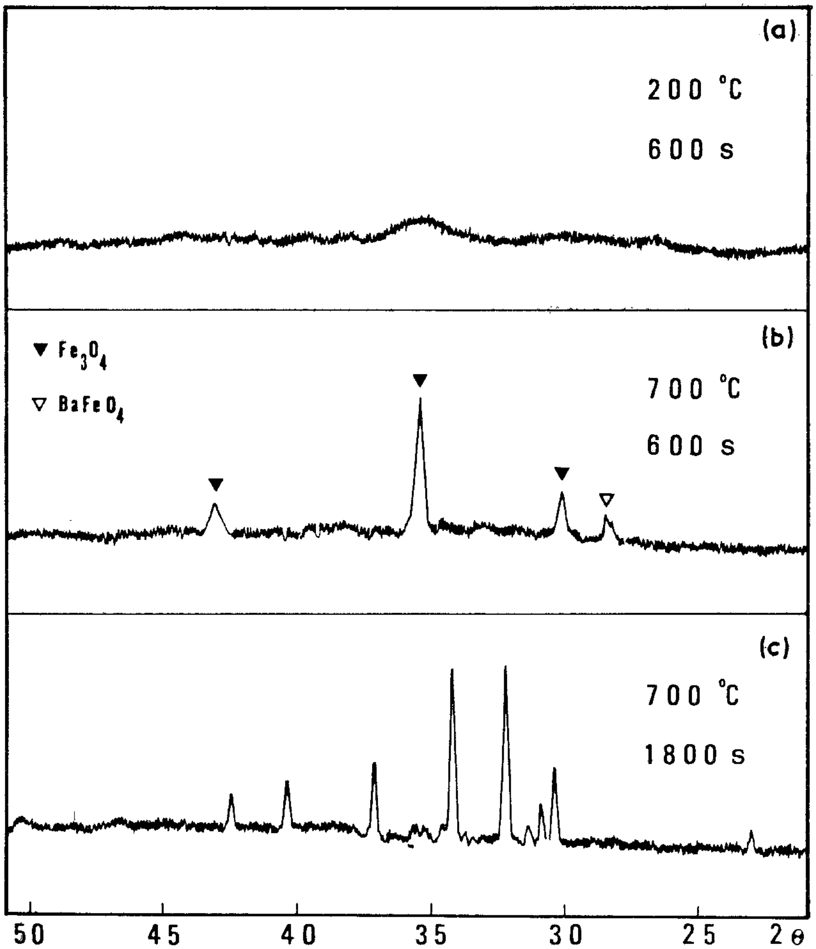

Figure 3 X-Ray diffraction patterns of the lyophilized gel heated (a) to 200° C and of the same material maintained at 700° C for (b) 10 min, and (c) 30 min.

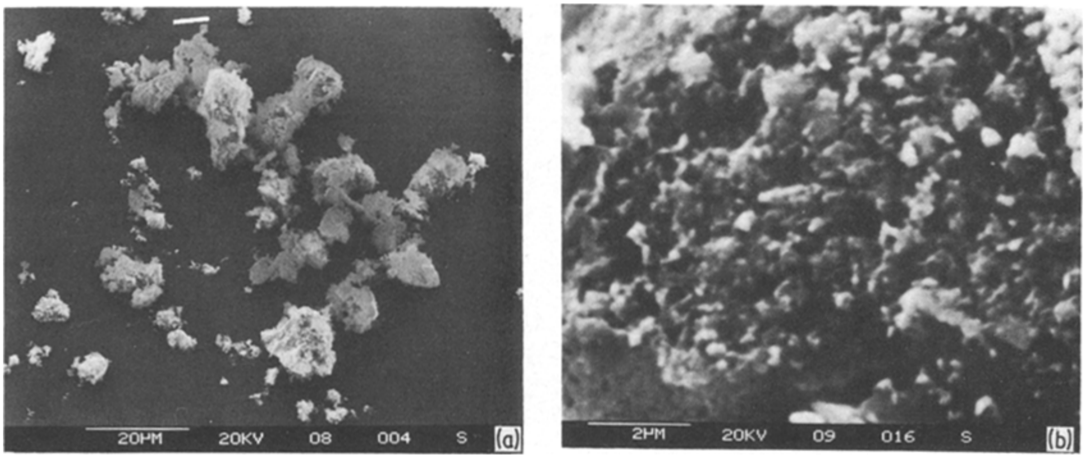

Figure 4 (a) Microaggregates of hexaferrite particles obtained by heating at 700° C for 30 min the pre-fired lyophilized gel. (b) As above, magnified ten times.

in air, cooled immediately after attainment of this temperature and subjected to X-ray diffraction analysis, showed the lines of the hexaferrite alone.

The size of the ferrite particles was determined with a scanning microscope. Fig. 4 presents SEM images of a sample prepared by heating at 700° C for 30 min a portion of the pre-fired lyophilized gel. It can be seen that the particles are definitely below 1 micron in size.

4. Conclusions

Starting from freeze dried gels composed of ammonium pectate and Ba^{2+} and Fe^{3+} salts, hexaferrite powders can be obtained at low temperatures. The rate of $Ba0.6Fe_2O_3$ formation at 600° C is controlled by the oxidation of the Fe^{2+} ions formed during the combustion of the organic matter. For samples fired in an oxygen atmosphere, after 22 h the X-ray diffraction analysis showed only the lines due to the hexaferrite. The same result was obtained at 700° C in air after 20 min. At 800° C the formation of the hexaferrite is practically instantaneous. Examination of the powders by means of the scanning electron microscope showed that particles less than 1 micron in diameter are obtainable by firing at temperatures about 700° C for controlled periods of time. Such particle size is a necessary condition for the attainment of high coercive forces.

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References

1. R. C. TENZER, *J. Appl. Phys.* **34** (1963) 1267.
2. G. C. BYE and C. R. HOWARD, *J. Appl. Biotechnol.* **21** (1971) 319.
3. F. J. ESPER and G. KAISER, *Ber. Dt. Keram. Ges.* **55** (1978) 294.
4. G. HEIMKE, *Z. Angew. Phys.* **15** (1963) 271.
5. K. HANEDA, C. MIYAKAWA and H. KOJIMA, *J. Amer. Ceram. Soc.* **57** (1974) 354.
6. A. HAUG and O. SMIDSRØD, *Acta Chem. Scand.* **24** (1970) 843.
7. O. SMIDSRØD and A. HAUG, *ibid.* **26** (1972) 79.
8. R. KOHN, *Pure Appl. Chem.* **42** (1975) 371.
9. F. HABEREY, M. VELICESCU and A. KOCKEL, *Int. J. Magn.* **5** (1973) 161.
10. C. OKAZAKI, S. MORI and H. MITSUDA, *Acta Crystallogr.* **16** (1973) 4.
11. S. MERIANI, *ibid.* **28** (1972) 1241.

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