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Molten salt synthesis of anisotropic $BaFe_{12}O_{19}$ powders

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The formation mechanism, morphology, and magnetic properties of anisotropic $BaFe_{12}O_{19}$ powders prepared by the 0.8 Na_2SO_4–0.2 K_2SO_4 molten salt synthesis have been investigated. The reaction can be completed at temperatures lower than 845 °C which is the melting point of the 0.8 Na_2SO_4–0.2 K_2SO_4 salt mixture, due to the presence of the low melting phase related to the formation of $BaSO_4$ and $Na_6CO_3(SO_4)_2$. Even at temperatures lower than 845 °C, with the aid of the low melting phase, the morphology of ferrites was thin platelets. Magnetic properties such as coercivity, saturation magnetization, and remanent force are comparable to those found in other processing techniques. The orientation degree of the sintered body was very high due to anisotropic morphology; thus powders from molten salt synthesis are suitable for grain oriented ceramics.

1. Introduction

Although having poor magnetic properties compared with $SmCo_5$, Sm_2O_{17}, or $Nd_2Fe_{14}B$, barium ferrite has been widely used as a ceramic permanent magnet or as a component of plastic magnets due to its chemical stability, wear resistance, and low cost. The necessity of using anisotropic barium ferrite powders has been increased because grain orientation is possible simply by a tape casting or normal pressing and sintering procedure. Many methods have been proposed for preparing anisotropic ferrites, such as chemical coprecipitation [1–3], electrolytic coprecipitation [4], liquid mix technique [5], hydrolysis of organometallic compounds [6–9], hydrothermal method [10], and glass crystallization [11] method.

Molten salt synthesis (MSS) has been used for the preparation of plate-like or needle-like powders of soft ferrites, plate-like powders of bismuth-layer structure compounds, such as $Bi_4Ti_3O_{12}$ and Bi_2WO_6, and needle-like powders of $PbNb_2O_6$. The anisotropic powders thus obtained are suitable for grain-oriented ceramics using simple pressing or tape casting.

Arendt [12] and Wickham [13] have used the MSS process for the preparation of barium ferrite powders. Arendt has prepared barium ferrite in 0.5 NaCl–0.5 KCl salts, and Wickham has used 0.8 Na_2SO_4–0.2 K_2SO_4 salts. According to Wickham, "In the system Na_2SO_4–K_2SO_4 the composition with the lowest melting point (845 °C) contains 80 mol % Na_2SO_4. The compounds $BaFe_{12}O_{19}$, $SrFe_{12}O_{19}$, and $CaFe_2O_4$ can be prepared with this salt mixture at 940 °C", but no information about formation mechanism, powder morphology, and magnetic properties is available. In this study, the formation reaction, powder morphology, and magnetic properties of barium ferrites obtained by the MSS process using a 0.8 Na_2SO_4–0.2 K_2SO_4 salt mixture have been studied.

2. Experimental procedure

2.1. Preparation of powders

The starting materials were Fe_2O_3 (99%), $BaCO_3$ (98%), K_2SO_4 (99.5%), and Na_2SO_4 (98%). The ratio of Ba/Fe in the reactants used was 1/6, and the composition of the salt mixture used was 0.8 Na_2SO_4–0.2 K_2SO_4 (m.p. 845 °C) (from now on, this composition of the salt mixture is called only the salt mixture). The mixtures of reactants and salt mixture were ball-milled for 6 h in ethanol with a steel ball-mill. The flux ratio, which is defined here by the ratio of total weights of salt mixture per total weights of reactants, was fixed at 1. The mixtures were heated in an alumina crucible with the heating rate of 600 °C h^{-1}, and then air-cooled. The salt mixtures were washed out with warm deionized water until the aliquot became free from salt anions as checked by $Ba(NO_3)_2$ solution, and the remaining powders were dried.

2.2. Characterization of powders

X-ray diffraction (XRD) and Fourier transform-infrared (FT-IR) spectra analyses were used for the identification of the products. The particle sizes and morphologies of the powders were observed by SEM. Differential thermal analysis (DTA) and thermogravimetry (TG) were conducted at a heating rate of 10 °C min^{-1}, and the specific surface areas of the powders were measured by the BET method (Disisorb 2000, Micrometrics). Chemical analysis of the remaining salts after washing was conducted by atomic absorption spectrophotometry (AA), inductively coupled plasma spectrometry (ICP), and the wet-chemical method. The magnetic properties were measured with a vibrating sample magnetometer at room temperature.

3. Results and discussion

3.1. Formation mechanism

Fig. 1 shows XRD patterns of powders obtained at various reaction temperatures. XRD patterns of the powder obtained at 650 °C showed the presence of Fe_2O_3, small amounts of $BaFe_{12}O_{19}$ and an unknown phase. It is surprising that small amounts of $BaFe_{12}O_{19}$ were found before the melting temperature of this salt mixture, 0.8 Na_2SO_4–0.2 K_2SO_4, and the unknown phase was not one of the reported second phases of BaO and Fe_2O_3. However, at higher temperatures, there was only Fe_2O_3 and $BaFe_{12}O_{19}$. In addition, the fact that an appreciable amount of ferrite was formed below 845 °C indicates that there may be a reaction between the reactants and the salt mixtures to form a low-melting flux. Above 850 °C (Fig. 1e and g) there was no Fe_2O_3, and the only remaining phase was $BaFe_{12}O_{19}$. Therefore, the MSS process yields a much lower formation temperature of $BaFe_{12}O_{19}$ (at about 850 °C) than the conventional ceramic processing in which the complete ferrite formation temperature is 950 °C.

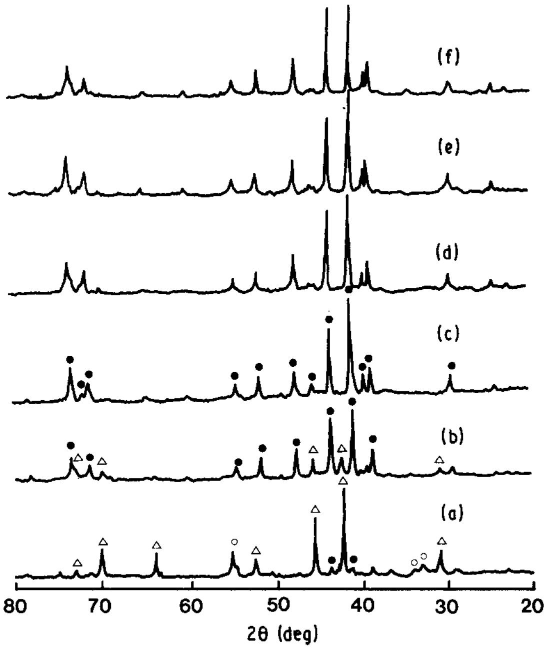

Figure 1 XRD (FeK_α) patterns of powders obtained at various temperatures for 1 h (after washing). (●) $BaFe_{12}O_{19}$, (△) Fe_2O_3, (○) unknown phase. (a) 650 °C, (b) 700 °C, (c) 750 °C, (d) 800 °C, (e) 850 °C, (f) 950 °C.

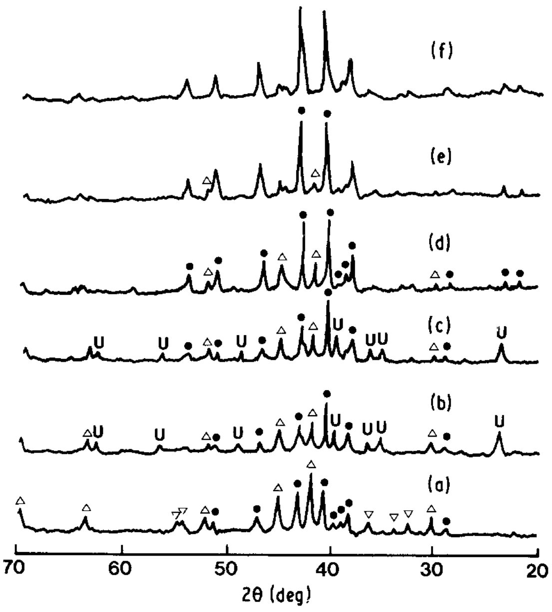

Figure 2 XRD (FeK_α) patterns of powders obtained at 700 °C for various reaction temperatures (after washing). (●) $BaFe_{12}O_{19}$, (△) Fe_2O_3, (▽) $BaSO_4$, (U) unknown phase. (a) 30 min, (b) 45 min, (c) 60 min, (d) 90 min, (e) 120 min, (f) 180 min.

Fig. 2 shows XRD patterns of powders at 700 °C for various reaction times. For a reaction time of 30 min (Fig. 2a) $BaSO_4$ was observed; therefore, we can conjecture that the reaction between $BaCO_3$ and the salt mixture can occur, and this may be related to the low-melting phase. For longer times (Fig. 2b, c) the unknown phase was observed, and there was no $BaSO_4$ phase present. For a reaction time of 180 min (Fig. 2g) there was almost complete ferrite formation, and this gives confirmation that there was a low-melting phase below the melting of the salt mixture at 845 °C.

In order to clarify the formation mechanism of $BaFe_{12}O_{19}$ in the salt mixture, DTA/TG was conducted for mixtures of 0.4211 Na_2SO_4–0.1053 K_2SO_4–0.0677 $BaCO_3$–0.4059 Fe_2O_3 (Fig. 3a) and 0.7089 Na_2SO_4–0.1772 K_2SO_4–0.1139 $BaCO_3$ (Fig. 3b).

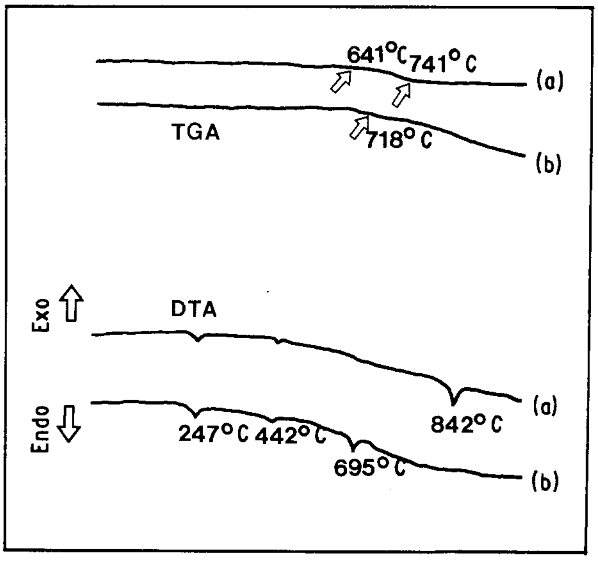

Figure 3 DTA/TGA results of 0.4211 Na_2SO_4–0.1053 K_2SO_4–0.0677 $BaCO_3$–0.4059 Fe_2O_3 and 0.7089 Na_2SO_4–0.1772 K_2SO_4–0.1139 $BaCO_3$.

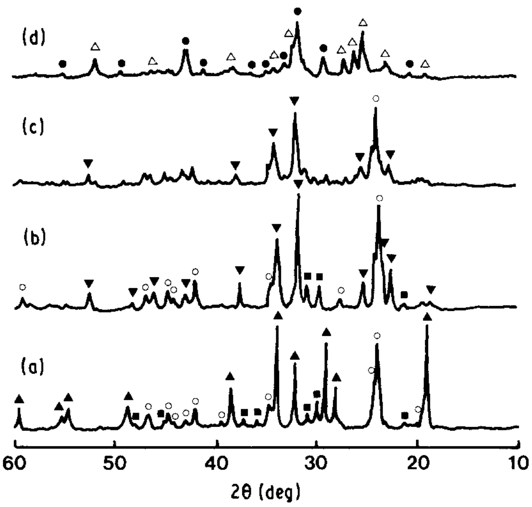

Figure 4 XRD patterns of 0.7089 Na_2SO_4–0.1772 K_2SO_4–0.1139 $BaCO_3$ at (a) 25 °C, (b) 300 °C for 15 min, (c) 450 °C, (d) 740 °C for 30 min. (△) $Na_6CO_3(SO_4)_2$, (●) $BaSO_4$, (▼) Na_2SO_4 (h), (■) K_2SO_4, (▲) Na_2SO_4, (○) $BaCO_3$.

From the XRD results (Fig. 4), the peak at 247 °C was due to the phase transformation of Na_2SO_4 to its high-temperature form. To assign the peaks at 442 and 695 °C, XRD and FT–IR analyses were performed. XRD patterns (Fig. 4c) showed the presence of $BaSO_4$ and $Na_6CO_3(SO_4)_2$. Therefore, this reaction can be considered to be as follows:

$$BaCO_3 + 3\,Na_2SO_4 \rightarrow BaSO_4 + Na_6CO_3(SO_4)_2 \quad (1)$$

This is a simple anion exchange reaction, and the preservation of carbonates can be verified by the fact that there is no weight loss on TG and no reduction of peak intensity of the carbonates about 1500 cm^{-1} of FT–IR spectra of Fig. 5c.

The peak at 695 °C was assigned as a formation of a liquid phase related to $BaSO_4$, $Na_6CO_3(SO_4)_2$, and other salts, because of *in situ* observation of the presence of the liquid phase. The weight loss from 718 °C (Fig. 3b) was due to the evaporation of the carbonates because the FT–IR spectra (Fig. 5d) indicate that the carbonate peak intensity was decreased. Thus the weight loss between 641 and 741 °C (Fig. 3a) was assigned to the carbonate evaporation accompanying the ferrite formation. Thus, we propose the formation mechanism of barium ferrite in the salt mixture as follows

$$\begin{aligned}
&3\,Na_2SO_4 + BaCO_3 + 6\,Fe_2O_3 + \text{remaining salts}\\
&\quad\rightarrow Na_6CO_3(SO_4)_2 + BaSO_4 + 6\,Fe_2O_3\\
&\qquad + \text{remaining salts}\\
&\quad\rightarrow \text{unknown phase} + CO_2 + BaFe_{12}O_{19}\\
&\qquad + x\,Fe_2O_3 + \text{remaining salts}\\
&\quad\rightarrow BaFe_{12}O_{19} + \text{remaining salts}
\end{aligned}$$

The identification of this unknown phase is now under investigation.

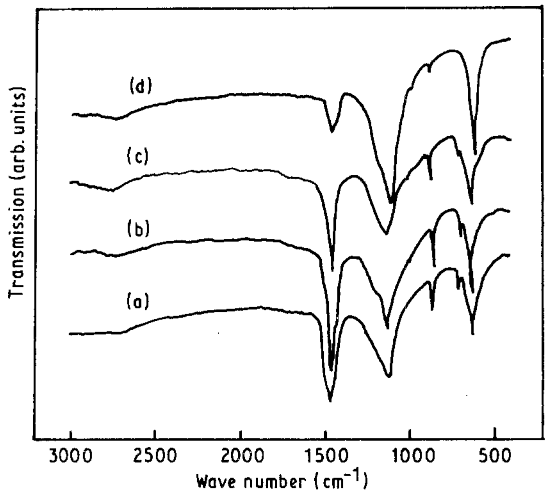

Figure 5 FT–IR spectra of 0.7089 Na_2SO_4–0.1772 K_2SO_4–0.1139 $BaCO_3$ at (a) 25 °C, (b) 300 °C for 15 min, (c) 450 °C, (d) 740 °C for 30 min.

3.2. Morphology

Fig. 6d is the SEM of the ferrite powders obtained by solid state reaction at 1250 °C for 1 h. As shown, no anisotropic powders could be obtained by a solid state reaction. Fig. 6a–c show the morphologies of the powders obtained at various temperatures by the MSS. At 800 °C agglomerated hexagonal platelets were developed by the low-melting flux. Above 800 °C, discrete platelets are found, hence the ferrite formation stage and particle growth stage are thought to be separated. It is surprising that at temperatures below 845 °C, which is the melting point of the salt mixture, hexagonal platelets are developed with the aid of the low-melting phase which is shown to be related to the formation of $BaSO_4$, $Na_6CO_3(SO_4)_2$, and the unknown phase. Fig. 7 shows the effect of reaction time on morphology. At lower temperatures, about 700 °C, agglomerated particles did not change into discrete particles on further heating (Fig. 7a, b), but at higher temperatures they changed into discrete particles of about 1–1.5 μm.

Wickham [13] did not mention any side reactions, but we discovered that in this case a side reaction between the reactant and salt is not harmful; rather, it is very favourable for obtaining anisotropic powders at very low temperatures. Thus, when using this salt mixture, anisotropic $BaFe_{12}O_{19}$ powders with controlled particle sizes can be obtained at about 700–800 °C.

3.3. Magnetic properties and the possibility of grain orientation

Several washings with warm deionized water are enough to remove salts, and maximum amounts of the remaining salts after washing were 0.03 wt %, hence their effects are thought to be negligible on magnetic properties and sintering behaviour. Figs 8–10 show fairly good magnetic properties. Above 850 °C, at which complete ferrite formation occurs, there is almost no increase in magnetic properties. These values are comparable to those from other processing techniques. Powders without binders were pressed at 4.7 ton cm^{-2}, and then sintered at 1300 °C for 3 h. The powders used were solid-salt reacted powders at 1250 °C for 1 h and molten-salt synthesized powders at

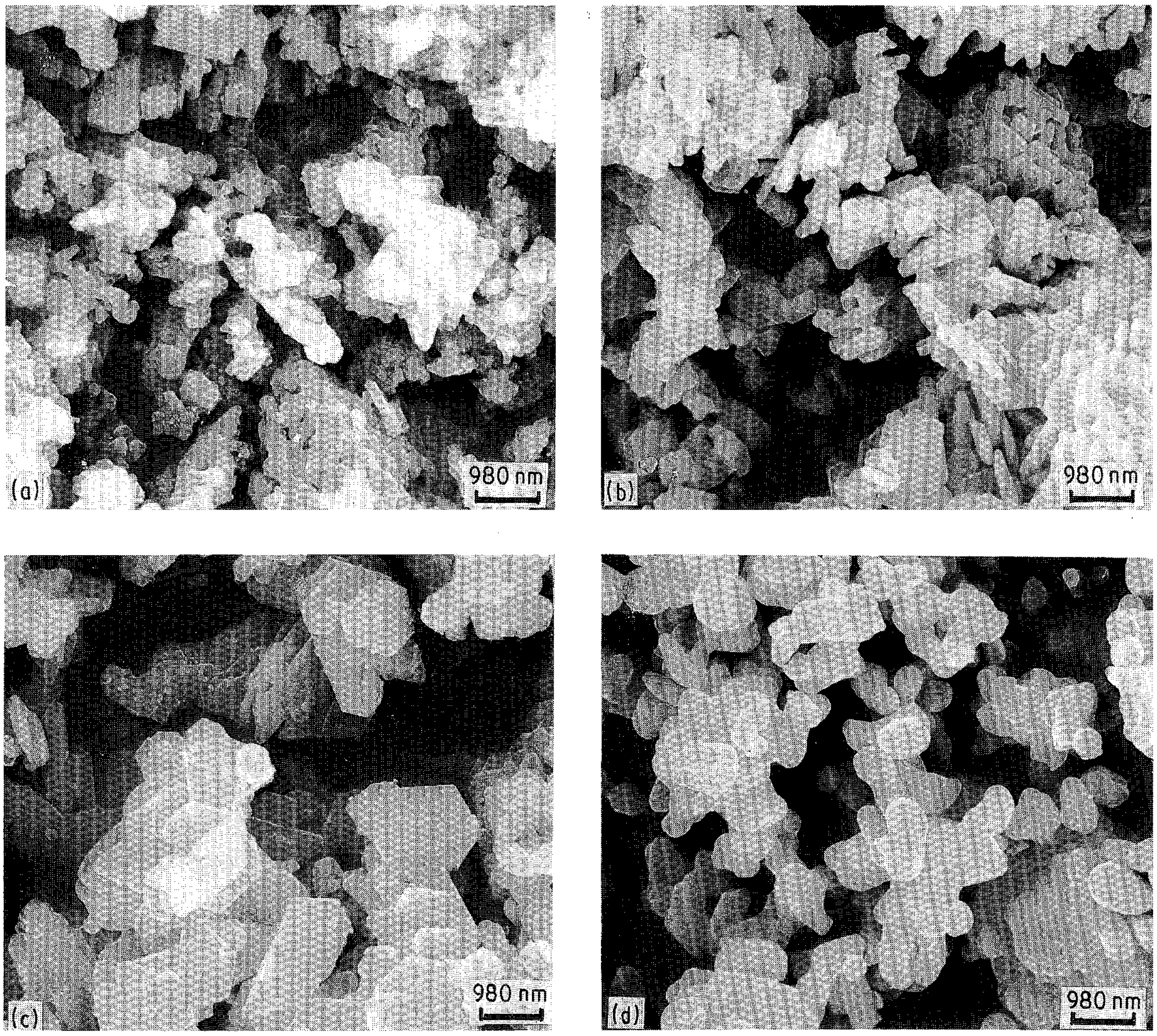

Figure 6 Scanning electron micrographs of powders obtained in the flux at (a) 700 °C, (b) 800 °C, (c) 900 °C for 1 h (after washing), and of (d) solid-state reacted powders obtained at 1250 °C for 1 h.

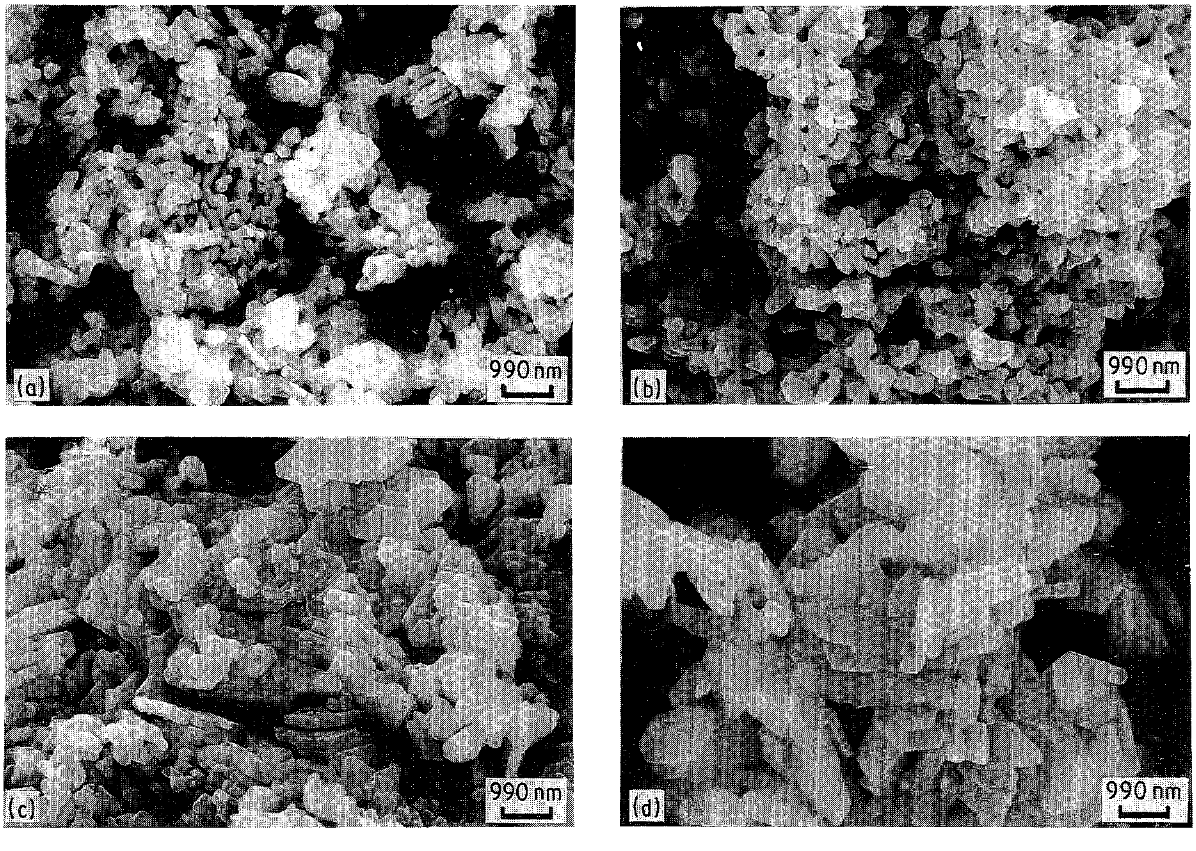

Figure 7 Scanning electron micrographs of powders obtained in the flux for (a) 4 h, (b) 5 h at 700 °C, (c) 1 h, (d) 22 h at 750 °C (after washing).

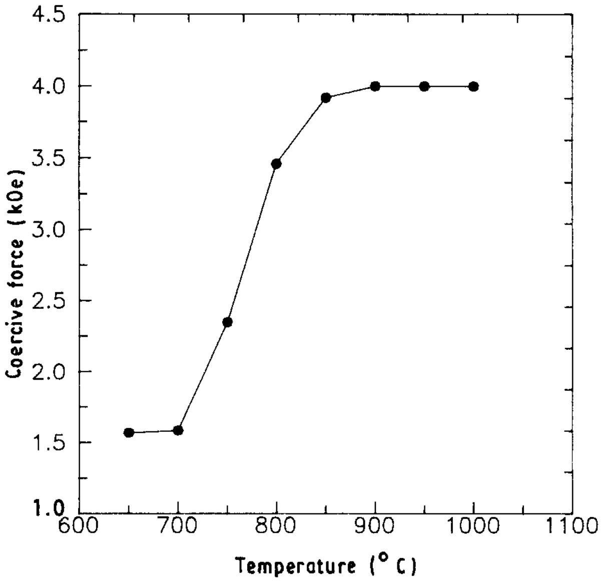

Figure 8 Reaction temperature versus coercivity.

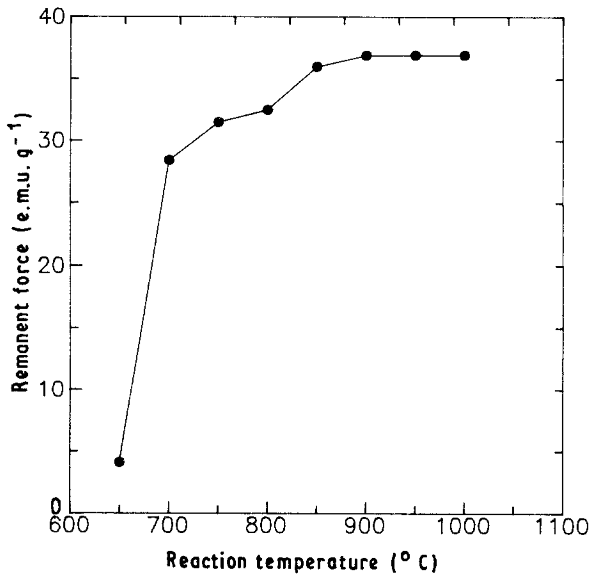

Figure 9 Reaction temperature versus remanent force.

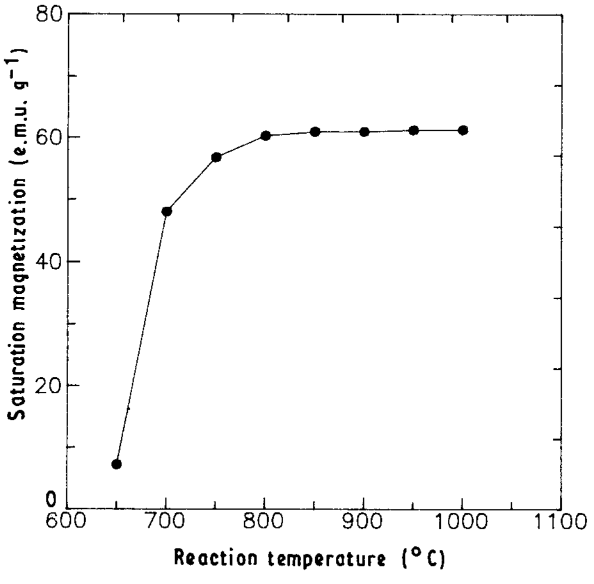

Figure 10 Reaction temperature versus saturation magnetization.

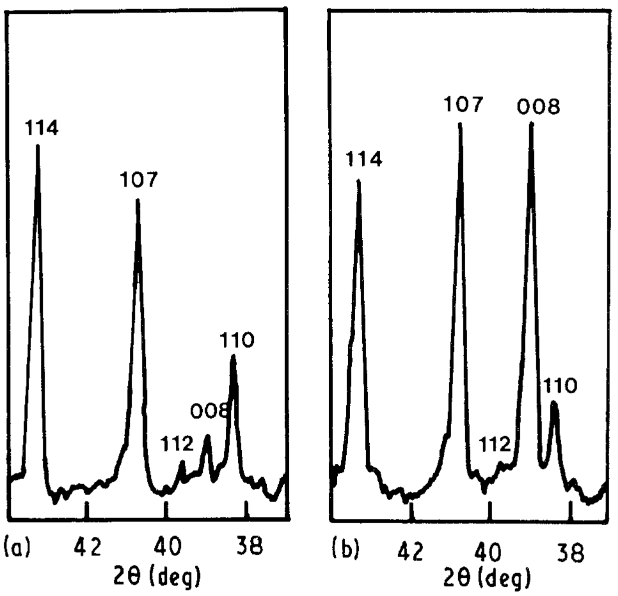

Figure 11 XRD patterns of sintered bodies prepared by (a) solid-state reaction, (b) the MSS process.

900 °C for 1 h. Fig. 11 shows the XRD patterns of sintered bodies prepared by a solid-state reaction and the MSS process. A sintered body prepared by the MSS process shows a more than seven times intense (0 0 8) peak intensity compared with a sintered body prepared by a solid-state reaction, due to the alignment of particles perpendicular to the *c*-axis.

4. Conclusions

The reaction can be completed at temperatures lower than 845 °C which is the melting point of 0.8 Na_2SO_4–0.2 K_2SO_4 salt mixture, due to the presence of the low-melting phase related to the formation of $BaSO_4$ and $Na_6CO_3(SO_4)_2$. Powders obtained by the MSS process are thin hexagonal platelets of about 1–1.5 μm, thus by a normal pressing and sintering procedure, the sintered body of these powders shows a high *c*-axis orientation.

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