Chemical processing of sodium doped hexagonal Sr-ferrite: Part IV—Microstructural and magnetic studies

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The effects of sodium ions added before and after calcination of coprecipitated hexagonal Sr-ferrite are investigated. The values of important performance parameters, namely, energy product \((BH)_{\text{max}}\), remanence \((B_r)\) and coercivity \((H_c)\) are significantly improved when sodium ions are added after calcination. The better magnetic properties are assigned to the improved microscopic (structural and chemical) homogeneity and sintered density.

The employment of wet chemical methods for the synthesis of hexagonal ferrite powders is of current interest. It allows a high degree of micro-homogeneity and improved sinterability of the green compacts. A number of chemical and ultrastructural processing techniques are being developed and perfected which enable easier synthesis of powders of well-defined compositions with high purity, close control of composition and excellent compositional homogeneity at sufficiently low temperatures. In our earlier work, optimization of various processing parameters was studied to achieve better performance parameters for the hexagonal Sr-ferrite compacts. It was also noticed that the ‘better’ functional microstructure is extensively controlled by the small amount of residual sodium ions left behind during the various processing stages. To obtain better compacts on a reproducible basis, addition of optimum amount of sodium ions after the calcination of the coprecipitate around 700°C in air was found to improve the sintered density \((D)\) and related magnetic performance parameters \((H_c, H_e, (BH)_{\text{max}})\). Microstructural aspects, i.e., shape, size and the distribution of microcrystallites, porosity/relative density have been studied using XRD, SEM/EPMA techniques. The magnetic parameters were also measured using B–H loop tracer. In this paper, the magnetic and microstructural behaviour for the series of dense compacts of Sr-ferrite are presented.

Materials and Methods
Polycrystalline strontium ferrite \((\text{SrFe}_{12}\text{O}_{19})\) was synthesized by chemical coprecipitation method using \(\text{FeCl}_3.6\text{H}_2\text{O}\) \((2.6 M)\) and \(\text{SrCl}_2.6\text{H}_2\text{O}\) \((1.2 M)\) solutions with \(\text{NaOH}\) \((5.1 M)\) solution as the precipitating agent, all these reagents being AR grade chemicals. \(\text{Fe}/\text{Sr}\) ratio was kept 10.6/1. The details of the method are reported in the earlier papers published from our laboratory. The washed and dried coprecipitate prepared by the procedure described in part III of this series was used for doping of sodium ions at the two stages of preparation, namely, before and after calcination of ferrite powders. Two batches of coprecipitate on 50 g scale were prepared for this purpose. The first batch coprecipitate was divided into two equal parts which were processed as per the flow sheet shown in Fig. 1a to prepare ferrite samples A255 and A305. The second batch coprecipitate was directly calcined at 750°C for 5 h and then divided into two parts. They were treated as per flow sheet shown in Fig. 1b to get ferrite samples A2 and A21. From the flow sheets, it is clear that ferrite samples A255 and A2 are obtained by direct calcination of the coprecipitate while ferrite samples A305 and A21 are doped with Na ions (0.5% and 0.4% by weight) before and after calcination stages respectively. The two undoped samples A255 and A2 were prepared for
comparative evaluation of magnetic performance of their doped counterparts from the respective batches.

Pressing and sintering

The ferrite powder samples were mixed with 1% solution of polyvinyl alcohol as a binder and then pressed into pellets of 1.5 cm diameter and 0.5 cm thickness by applying a pressure of 2.2 tons/cm². The green pellets were sintered at 1130°C for 2h in air to get sintered ferrite compacts.

Physicochemical characterization

Doped as well as undoped ferrite samples were characterized at various stages of processing by different physicochemical techniques for understanding their structural, microstructural and magnetic properties as described below.

(i) XRD—Ferrite formation in the calcined powders was detected by powder X-ray diffraction using Philips PW 1730 diffractometer with CuKα radiation (λ = 1.542Å). XRD patterns of coprecipitate, undoped and doped ferrite powders and of sintered compacts are given in Fig. 2 (a,b,c,d).

(ii) SEM/EPMA—Scanning electron microscopy (SEM) and electron probe micro analysis (EPMA) (Hitachi Model No. H-8010 coupled with Kevek analyst 8000 microanalyser) of these samples were carried out at the Department of Applied Chemistry of Gifu University, Japan. Sr-ferrite in the form of crushed compacts was analysed by SEM/EPMA. SEM photographs were recorded for different regions of the sample. EPMA analysis was carried out at different points and areas mainly for atomic percentage of Na, Sr and Fe. SEM photographs are given in Fig. 3 (a,b,c,d) and EMPA analysis results in Tables 1-4.

(iii) Magnetic measurements—B-H loops of the sintered ferrite compacts were traced using B-H Loop tracer of Walker Scientific, model MH 1020. From B vs H and (B-H) vs H loops, magnetic performance parameters such as remanence...
Results and Discussion

(1) XRD—The XRD pattern of dry coprecipitate of mixed hydroxides shows the presence of $\alpha$-Fe$_2$O$_3$, $\alpha$-Fe$_3$O$_4$, H$_2$O and SrCO$_3$ (Fig. 2a). The presence of these oxides and hydrated oxides is due to the conversion of unstable Fe(OH)$_3$ into the corresponding oxides. The presence of SrCO$_3$ is due to the formation of SrCO$_3$ from Sr(OH)$_2$ by the absorption of CO$_2$ from the ambient air which is expected of an alkaline earth metal like strontium. XRD pattern of calcined sample A255 (Fig. 2b) shows the prominent lines of the hexagonal Sr-ferrite ($\text{SrFe}_{12}\text{O}_{19}$) phase at $2\theta = 32.3^\circ$ and $34.2^\circ$ matching with reported data$^{13}$. In addition, the lines corresponding to $\alpha$-Fe$_3$O$_4$ are clearly seen and a weak line of SrCO$_3$ also shows its presence. XRD data clearly indicate the initiation of the ferritization reaction at 750°C in conformity with our thermal data reported earlier$^8$. Figure 2c shows XRD pattern of doped Sr-ferrite sample A305. It shows that the intensities of Sr-ferrite peaks have considerably increased and those of $\alpha$-Fe$_3$O$_4$ have decreased to a large extent as compared to those of sample A255. This is indicative of the increase in the extent of formation of Sr-ferrite phase due to the doping of Na ions. Single phase Sr-ferrite is obtained on sintering the green sampes at 1130°C for 2h (Fig. 2d).

XRD patterns of ferrite samples A2 and A21 are almost identical since the dopant concentration in A21 is 0.4% by wt which is well below the detection limit of the instrument.
(2) Microstructure and magnetic properties
(A) Samples A255 and A305

Figure 3a shows heterogeneous particle distribution in sample A255. Size of the particle is much bigger, ranging from 2 to 10 \( \mu \text{m} \). Small and big voids are also seen in the SEM photograph. On the other hand, the grain distribution in the sample A305 is homogeneous and comparatively smaller grains of 2 to 4 \( \mu \text{m} \) are seen along with a few small voids (Fig. 3b).

These observations reveal the effect of sodium ion doping (before calcination) on Sr-ferrite compacts. The difference in microstructure has resulted in different magnetic performance parameters given in Table 5. A comparative evaluation of magnetic properties of A255 and A305 samples is presented below.

Sample A255 (undoped)
(i) Inhomogeneous grain size and its distribution led to comparatively low values of \( \mu H_c \) and \( H_c \) namely 1550 and 3150 Oe respectively.
(ii) The low densification (4.43 g cm\(^{-3}\)) could be explained on the basis of presence of voids resulting in the decrease of remanence (\( B_r \)) to 2100 Gauss.
(iii) Fe/Sr ratio varies from 11.6 to 32.9 as against the expected value between 11 and 12. The broad range of this ratio implies chemical inhomogeneity at microstructural level.

Sample A305 (doped)
(i) Homogeneous grain distribution and smaller grain size as compared to undoped sample A255 is responsible for comparatively higher values of coercivities (\( \mu H_c = 1850 \text{ Oe} \) & \( H_c = 3300 \text{ Oe} \)) achieved on Na-doped ferrite sample.
(ii) Increase in remanence value to 2600 G is attributed to increase in sintering density (4.58 g cm\(^{-3}\)) obtained due to less number of voids and better compaction of grains.
(iii) Fe/Sr ratio is between 11.4 and 15.5 which is indicative of chemical homogeneity at microscopic level which again may be due to Na ion doping.

(B) Samples A2 and A21
It is rather difficult to study the grain size and its distribution since the SEM photograph (Fig. 3c) is taken on higher scale (10 \( \mu \text{m} \)). Moreover, different scales are used for samples A2 and A21 (Fig. 3d) so that it is difficult to compare their microstructures.

However, EPMA analysis (Table 3) and magnetic properties (Table 5) of sample A2 may be correlated as follows. The Fe/Sr ratio varies from 2.9 to 14.7 indicating higher percentage of strontium as compared to that of iron except for the ratio 14.7. It indicates chemical inhomogeneity at microscopic level. Therefore, magnetic properties of the sample are poor and nearly equal to those of Sr-ferrite compacts prepared by solid state synthesis\(^7\). The low value of remanence (\( B_r = 2100 \text{G} \)) is due to low sintered density (4.40 g cm\(^{-3}\)) of undoped sample A2.

For doped sample A21, the scale used for SEM photograph (Fig. 3d) is 15 \( \mu \text{m} \) and it is difficult to find out the grain size and distribution from the recorded micrograph. However, we get some important clues from EPMA results (Table 4) about its magnetic performance parameters (Table 5). Fe/Sr ratio lies between 12.9 and 14.4 which implies improvement in chemical homogeneity at microscopic level. Better magnetic properties are due to higher densification and improved homogeneity of the sample. The remanence increases from 2100 G to 2400 G which is attributed to higher density (4.65 g cm\(^{-3}\)) achieved for doped sample A21. Thus the magnetic performance parameters of the Sr-ferrite samples doped with Na ions (after\(^{12}\) or even before calcination) are superior to those of Na\(_2\)O doped Ba-ferrite as reported by Yung-Tsen \( et \) \( al \).\(^{14}\)

Thus, SEM/EPMA results obtained for sodium ion doping in Sr-ferrite, either before or after calcination, indicate that Na ion addition is responsible for better chemical homogeneity, higher densification and uniform microstructure of ferrite compacts. Consequently, uniform microstructure
with a narrow range of grain size avoids large demagnetizing fields and results in improved magnetic performance parameters of Sr-ferrite magnets.

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References