Abstract—Strontium hexaferrite (SrFe$_{12}$O$_{19}$, Sr-ferrite) is one of the well-known materials for permanent magnets. In this study, M-type strontium ferrite was prepared by following the conventional ceramic method from steelmaking by-product. Initial materials; SrCO$_3$ and by-product, were mixed together in the composition of SrFe$_{12}$O$_{19}$ in different Sr/Fe ratios. The mixtures of these raw materials were dry-milled for 6h. The blended powder was pre-sintered (i.e. calcination) at 1000°C for different times periods, then cooled down to room temperature. These pre-sintered samples were re-milled in a dry atmosphere for 1h and then fired at different temperatures in atmospheric conditions, and cooled down to room temperature. The produced magnetic powder has a dense hexagonal grain shape structure. The calculated energy product values for the produced samples ranged from 0.3 to 2.4 MGOe.

Keywords—Ceramic route, Hard magnetic materials, Strontium ferrite.

I. INTRODUCTION AND BACKGROUND

MAGNETIC materials market is forecast to witness a significant increase in demand, driven by the evolution of new end-use applications, and consistent demand from existing end-use markets, including industrial and consumer electronics, data storage, military and aerospace, medical, power generation, and telecommunications. New technological innovations, improved electrical, magnetic, and mechanical performance of soft and hard magnetic materials, and represent the major factors influencing demand for magnetic materials [1], [2].

During the twentieth century, several permanent magnet materials were discovered. Techniques to effectively manufacture these magnets have been established. Device designs using such magnets in various active and passive applications have been successfully exploited. The energy product, which is a key figure of merit of permanent magnets, has been enhanced, starting from $\approx 1$ MGOe for steels discovered during the early part of the century, increasing to $\approx 3$ MGOe for hexagonal ferrites [3].

Magnetic materials are widely used as components in various applications of industrial and medical equipment. A very well-established class of magnetic materials is made from magnetic ceramic materials, or ferrites [4]-[6], which are essential in devices for storing energy in a static magnetic field. Major applications involve the conversion of mechanical to electrical energy. The applications of magnetic materials in information technology have been growing continuously [7].

The ferrite materials may be classified into three different classes; spinel ferrites, garnet ferrites and hexagonal ferrites [8]. The magnetic spinel has the general formula of MFe$_2$O$_4$, where M is the divalent metal ion, usually Ni, Co, Mn, or Zn.

During the last few years spinel ferrites have drawn a major attention because of their technological importance in magnetic recording, magnetic fluid and catalyst. The garnet ferrites are the basis of materials for many high-technology devices for magneto-optic, microwave and memory applications [6]. The ferrites used for permanent-magnet purposes are the hexagonal ferrites, also called hard ferrites or M-type ferrites. For many applications a permanent magnet is the best choice because it provides a constant field without the continuous expenditure of electric power and without generation of heat. In 1952 this class of ferrite having permanent magnetic properties was discovered. These were the so-called hexagonal ferrites with formula M(Fe$_{12}$O$_{19}$) where M is usually barium Ba, Strontium Sr or Lead Pb [9]-[11].

Strontium hexaferrite (SrFe$_{12}$O$_{19}$, Sr-ferrite) is one of the well-known materials for permanent magnets. The magnetic properties of sintered Sr-ferrite depend on its microstructure (size and shape of the particles). In order to fabricate a sintered magnet with superior properties it is necessary to inhibit the grain growth during sintering and also to keep the microstructure homogeneous [12], [13].

The hard magnet with high coercivity, originates from high magnetocrystalline anisotropy with single easy magnetization axis [14]. It has been recognized that it can be used as permanent magnets such as recording media, telecommunication, and as components in microwave, higher-frequency, and magneto-optical devices [15]-[18]. It is also used as a dielectric or magnetic filler in the electromagnetic attenuation materials (EAM). EAM are used to minimize the electromagnetic interference (EMI), a specific type of environmental pollution. EMI has a serious problem due to huge growth in the utilization of electrical and electronic devices in the industrial, commercial and military applications [19]. Sr-ferrite powders are ideal fillers for the development of EAM due to their low cost, high stability, large electrical resistivity and high microwave magnetic loss.
Various processing techniques have been employed for fabrication of the Strontium ferrites, including the traditional sol–gel process [20], [21], the solid-state method [22], the salt melting method [23], ball milling [24], [25], self-propagating high temperature synthesis [26], and the chemical co-precipitation method [27]. However, the simple ceramic process has been extensively used in industrial manufacturing [28].

II. EXPERIMENTAL WORK

A. Raw Material

Strontium carbonate SrCO$_3$ (99% purity) and steelmaking by-product Iron oxide were used for the production of permanent magnet in the experiments. The Iron oxide samples were characterized with X-ray diffraction analysis (XRD), X-ray fluorescence (XRF) and Scanning electron microscope (SEM). It was found that iron oxide (Fe$_2$O$_3$) is about 93% purity. For SEM the sample to be examined was fixed directly on adhesive tape and then examined under scanning microscope. The SEM photos for iron oxide samples are shown in Figs. 1 (a) and (b). It was observed that grain coalescence with very low micropores and many macropores took place in a dense structure.

![SEM micrographs of iron oxide](image)

Fig. 1 SEM micrographs of iron oxide

B. Experimental System

In this study, M-type strontium ferrites were prepared by the conventional ceramic method. The initial materials, SrCO$_3$ and Iron oxide were mixed together in the composition of SrFe$_{12}$O$_{19}$ in different Sr/Fe ratios 1/12, 1/11 and 1/10. The mixtures of these raw materials were dry-milled for 6 h. The blended powder was pre-sintered (calcination) at 1000°C for 4, 8 and 12 h, then cooled down to room temperature. These pre-sintered samples were re-milled in a dry atmosphere for 1 h and then fired at 1100, 1200 and 1300°C for 2, 4 and 6 h in air atmosphere, and cooled down to room temperature.

The produced magnetic powder was characterized with X-ray diffraction analysis (XRD), X-ray fluorescence (XRF), and scanning electron microscope (SEM). The Magnetic properties including Coercivity (Hc), Magnetic saturation (Ms), and Magnetic remnance (Mr) were measured by vibrating sample magnetometer (VSM) for all samples as shown in Figs. 3 (a), (b), and (c) respectively. It can be seen that the measured magnetic values are in narrow range irrespective the different reaction conditions for these samples. Also the measured magnetic values at 300 and at 4.2 K are very close to each other that reflect excellent magnetic behavior. The value of the energy product ($BH$) which is representative of the energy required to demagnetize a permanent magnet is calculated comparatively for all the prepared samples.

III. RESULTS AND DISCUSSION

The XRD pattern for fired samples is shown in Fig. 2. It was observed that after calcination at 1000°C for 12 hrs, and then firing at 1100°C for 2 h, strontium carbonate decomposed to SrO and Strontium ferrite phase is completely formed.

![XRD pattern for iron oxide/strontium oxide mixture after calcination at 1000°C for 12 hrs and then firing at 1100°C for 2 hrs](image)

Fig. 2 XRD pattern for iron oxide/strontium oxide mixture after calcination at 1000°C for 12 hrs and then firing at 1100°C for 2 hrs

The magnetic properties including Coercivity (Hc), Magnetic saturation (Ms), and Magnetic remnance (Mr) were measured by vibrating sample magnetometer (VSM) for all samples as shown in Figs. 3 (a), (b), and (c) respectively. It can be seen that the measured magnetic values are in narrow range irrespective the different reaction conditions for these samples. Also the measured magnetic values at 300 and at 4.2 K are very close to each other that reflect excellent magnetic behavior. The value of the energy product ($BH$) which is representative of the energy required to demagnetize a permanent magnet is calculated comparatively for all the prepared samples.
The measured magnetic properties including Coercivity ($H_c$), Magnetic saturation ($M_s$), and Magnetic remanence ($M_r$) for all prepared samples were investigated. The influence of various parameters such as Sr/Fe mixing stoichiometry, calcination time, firing time and firing temperature on phase formation, microstructure and magnetic properties of the prepared Strontium ferrite were investigated.

### A. Influence of Mixing Stoichiometry

Strontium carbonate and iron oxide were mixed together in the composition of $\text{SrFe}_{12}\text{O}_{19}$ in different Sr/Fe ratios 1/12, 1/11 and 1/10 and then calcined at 1000°C for 12 hrs and then fired at 1200°C for 4 hrs. As shown in the XRD pattern (Fig. 4) the Sr-ferrite phase is successfully formed completely in the three samples. There are no peaks for unreacted $\text{Fe}_2\text{O}_3$ or SrO.

The grain size (1-3 μ) and grain shape of the synthesized strontium ferrite came very similar with well uniformed and homogeneous hexagonal crystalline shape as shown in Fig. 5. The magnetic values including Coercivity ($H_c$), Magnetic saturation ($M_s$), and Magnetic remanence ($M_r$) were measured for all samples at 300 and at 4.2 K. The value of the energy product ($BH$) is calculated comparatively for these samples. It was observed that the energy product increases with increasing the Sr/Fe ratios from 1/10 to 1/12 either at 300 or 4.2 K as shown in Fig. 6.

![Fig. 3 The measured magnetic properties including Coercivity ($H_c$), Magnetic saturation ($M_s$), and Magnetic remanence ($M_r$) for all prepared samples](image)

![Fig. 4 XRD pattern for iron oxide and strontium oxide mixed together in different Sr/Fe ratios 1/12, 1/11 and 1/10 and then calcined at 1000°C for 12 hrs and then fired at 1200°C for 4 hrs](image)

![Fig. 5 SEM micrographs for iron oxide and strontium oxide mixed together in different Sr/Fe ratios 1/12, 1/11 and 1/10 and then calcined at 1000°C for 12 hrs and then fired at 1200°C for 4 hrs](image)

![Fig. 6 Energy products values at 300 and 4.2 K for iron oxide and strontium oxide mixed together in different Sr/Fe ratios 1/12, 1/11 and 1/10 and then calcined at 1000°C for 12 hrs and then fired at 1200°C for 4 hrs](image)
B. Influence of Calcination Conditions

Strontium carbonate and iron oxide were mixed together in Sr/Fe ratio 1/12 and then calcined at 1000°C for 4, 8 and 12 hrs and then fired at 1200°C for 4 h. As shown in the XRD pattern (Fig. 7) it can be seen that the Sr-ferrite phase is successfully formed completely in the three samples. The grain size (1-3 µ) and grain shape of the synthesized strontium ferrite came very similar with well uniformed and homogeneous hexagonal crystalline shape as shown in Fig. 8. The value of the energy product (BH) was calculated comparatively for all samples at 300 and at 4.2 K. It was observed that the energy product increases with increasing the calcination time from 4 to 12 hrs at 300 or 4.2 K as shown in Fig. 9.

Fig. 7 XRD pattern for iron oxide and strontium oxide mixture after calcination at 1000°C for 4, 8 and 12 hrs and then firing at 1200°C for 4 hrs

Fig. 8 SEM micrographs for iron oxide and strontium oxide mixture after calcination at 1000°C for 4, 8 and 12 hrs and then firing at 1200°C for 4 hrs

A. Influence of Firing Time

Strontium carbonate and iron oxide were mixed together in Sr/Fe ratio 1/12 and then calcined at 1000°C for 12 h and then fired at 1100-1300°C for 2, 4 and 6 hrs. As shown in the XRD pattern (Fig. 10) for samples fired at 1200°C, it can be seen that at different reaction times the Sr-ferrite phase is successfully formed completely in the various samples. Also there are no peaks for unreacted Fe₂O₃ or SrO.

Fig. 9 Energy products values at 300 and 4.2 K for iron oxide and strontium oxide mixture after calcination at 1000°C for 4, 8 and 12 hrs and then firing at 1200°C for 4 hrs

Fig. 10 XRD pattern for iron oxide and strontium oxide mixture after calcination at 1000°C for 12 hrs and then firing at 1200°C for 2, 4 and 6 hrs

The morphological examination for these samples is shown in Fig. 11. There is no clear change in the grain size with increasing the firing time. Grain shape of the synthesized strontium ferrite came very similar with well uniformed and homogeneous hexagonal crystalline shape. The comparative values of the energy product (BH) were calculated for all samples at 300 and at 4.2 K. It was observed that the energy product increases with increasing the firing time up to 4 h but decreases again with increasing the reaction time to 6 h as shown in Fig. 12. It is believed that this behavior might be due to the formation of multi-domain and the easy movement of
the domain walls resulting in domains misalignment that decrease the energy product value after the saturation point.

![SEM micrographs for iron oxide and strontium oxide mixture after calcination at 1000°C for 12 hrs and then firing at 1200°C for 2, 4 and 6 hrs](image)

![Energy products values at 300 K for iron oxide and strontium oxide mixture after calcination at 1000°C for 12 hrs and then firing for 2, 4 and 6 hrs at 1200°C](chart)

![XRD pattern for iron oxide and strontium oxide mixture after calcination at 1000°C for 12 hrs and firing at 1100, 1200 and 1300°C for 2 hrs](chart)

A. Influence of Firing Temperature

Strontium carbonate and iron oxide were mixed together in Sr/Fe ratio 1/12 and then calcined at 1000°C for 12 h and then fired at 1100-1300°C for 2, 4 and 6 hrs. As shown in the XRD pattern (Fig. 13) for samples fired at 1100, 1200 and 1300°C for 2 h, it can be seen that at different reaction temperatures the Sr-ferrite phase is successfully formed completely in the various samples.

The morphological examination for these samples is shown in Fig. 14. The grain size is increased drastically with increasing the firing temperature from 1100 to 1300°C. Grain shape of the synthesized strontium ferrite became well crystalline hexagonal structure with increasing the firing temperature. The value of the energy product \((BH)\) was calculated comparatively for all samples at 300 and at 4.2 K. It was observed that the energy product increases with increasing the firing temperature up to 1200°C but decreases again with increasing the reaction temperature to 1300°C as shown in Fig. 15. This might be owing to the formation of multi-domain and the easy movement of the domain walls result in domains misalignment that decrease the energy product value.

![SEM micrographs for iron oxide and strontium oxide mixture after calcination at 1000°C for 12 hrs and then firing at 1100, 1200 and 1300°C for 2 hrs](image)

The comparative energy product values for all the prepared strontium ferrite samples at various reaction conditions showed that the highest energy product value for samples measured at 300 K is about 2.3 MGOe while for samples measured at 4.2 K is about 2.4 MGOe. These maximum energy product values are achieved by the same sample that was prepared with Sr/Fe ratio of 1/12, calcination at 1000°C for 12 h, and firing at 1200°C for 4 h.
Figure 15 Energy products values at 300 and 4.2 K for iron oxide and strontium oxide mixture after calcination at 1000°C for 12 hrs and then firing at 1100, 1200 and 1300°C for 2 hrs

IV. CONCLUSIONS

1. Hard magnetic material in powder shape (Sr-ferrite) was successfully synthesized through ceramic route using steel industry iron containing by-product

2. Hc, Ms and Mr were measured and energy product values were comparatively calculated for the various samples at 300 and 4.2 K

3. Hard magnetic characters enhanced gradually with:
   - Increasing the mixing ratio (Sr/Fe) up to stoichiometric ratio
   - Increasing the calcination time up to 12 h
   - Increasing the firing time up to 4 h
   - Increasing the firing temperature up to 1200°C

4. Similar energy product values were observed irrespective the measurement temperature to reflect excellent magnetic behavior.

5. The optimum energy product values were 2.3 and 2.4 MGOe at 300 and 4.2 K respectively

REFERENCES


