ABSTRACT:
As the information era continues to advance at a rapid pace, M-type strontium ferrite and other magnetic materials are finding more and more traditional uses. Numerous industries rely on it as a permanent magnet material because of its inexpensive cost, ease of preparation, and outstanding overall performance in areas including electronics, national defense, and communication. In this paper, we investigate some the magnetoelectric coupling properties at room temperature by solid phase method and sol-gel method. The phase structure was determined using an X-ray diffractometer, and the samples were all single-phase polycrystalline with a spatial group of P63/mmc. Observing the surface morphology using field emission scanning electron microscopy, it was found that the composition distribution of the samples prepared by solid-phase method was uneven and there was a "scandium rich phase". The samples prepared by the sol gel method have uniform composition distribution, hexagonal grain shape, and grain size of about 3-5 μ M. The magnetic properties of the samples prepared by the sol gel method and the solid phase method were studied, respectively. The results showed that the phase transition occurred in the solid phase method at about 250K, and the hysteresis loop at room temperature did not show the magnetoelectric coupling behavior. The magnetic phase transition of the sample prepared by the sol gel method occurred near 330K. Combined with the research on the hysteresis loops of the temperature above and below this phase transition point, it shows that this phase transition corresponds to the change of the ferromagnetic to the conical magnetic structure. The similar relationship between magnetic capacitance and magnetization intensity with magnetic field indicates that this conical magnetic structure can induce ferroelectric polarization, which can be understood based on the inverse Dzyaloshinskii-Moriya model.

Keywords: Hexagonal ferrite, sol gel method, conical magnetic structure, magnetic properties.
INTRODUCTION

Under policy guidance, China's manufacturing industries is gradually shifting towards a highly clustered and innovative development model. "Made in China 2025" clearly points out that "we should focus on ten key areas such as industries 4.0" [1,2,3]. In addition, the consistency evaluation of manufacturing industry 4.0, reform of the approval system, pilot implementation of the magnetic device marketing system, and other heavyweight policies and regulations have created a healthy and sustainable environment for the development of Chinese manufacturing enterprises [4,5,6].

Since the development of M-type barium ferrite developed by Phillips Laboratory in the 1950s, M-type strontium ferrite has also steadily developed [7]. Due to its high saturation magnetization, residual magnetism, Curie temperature, and good spin magnetism, as well as its high cost-effectiveness, it has been widely used in fields such as permanent magnets, high-density vertical magnetic recording, microwave and millimeter wave devices [8,9]. Although compared with most magnetic materials, the comprehensive magnetic properties of M-type strontium ferrite are relatively low, due to its abundant raw material resources, cheap price, mature preparation methods, excellent anti demagnetization and antioxidant properties. Therefore, M-type strontium ferrite remains an ideal magnetic material in many application fields, and in recent years, the development of M-type strontium ferrite has been flourishing.

At present, China is a major producer of permanent magnet materials, the production of high-performance permanent magnet ferrite accounts for a small share of the world’s total production [10]. The production technology of high-performance permanent magnet ferrite is still in the hands of developed countries, mainly due to the overall downturn of the domestic ferrite industry, outdated production equipment, and weak research and development capabilities, which directly leads to low product performance and technological content. However, in today's booming electronic industry, it is inevitable to drive the development of magnetic materials, and the high-performance ferrite industry naturally bears the brunt. Therefore, accelerating the research and development of high-performance ferrite is currently the primary task of China's ferrite industry.

Magnetic domains: Below the Curie temperature, several regions of spontaneous magnetization are formed within a large magnet, and the spontaneous magnetization in each independent region is uniform and consistent. Such each region is called a magnetic domain. Every small region is separated by magnetic domain walls, and the spontaneous magnetization generated inside the magnetic material needs to meet the principle of minimum energy to ensure vector balance. The formation of magnetic domains weakens the demagnetization energy of the magnetic material [11].

Magnetic crystal anisotropy: When permanent magnet materials are magnetized, the direction of the crystal axis is different, and the magnetization curve will also have significant differences. That is, the magnetic properties exhibit anisotropy with the change of the crystal axis direction, which is called magnetic crystal anisotropy [12]. Magnetic crystal anisotropy exists in all ferromagnetic crystals and is represented by the magnetic crystal anisotropy constants.

The room temperature single-phase strong magneto electric coupling material has aroused great interest among researchers. Single phase magneto electric coupling refers to the phenomenon where ferromagnetism and ferroelectricity coexist in the same material, and there is coupling between them. It has great potential for application in electrically written magnetic read memory, polymorphic memory, and sensors [13]. So far, only a few rooms temperature single-phase magneto electric coupling materials have been discovered, and the magneto electric coupling strength is mostly weak. At present, the most studied room temperature single-phase multiferroic materials include BiFeO₃ and its based compounds [14] and hexagonal ferrite [15]. In recent years, the magneto electric coupling effect caused by the conical magnetic structure of hexagonal ferrite has attracted great interest from researchers.
The preparation method of the sample has a significant impact on the electrical properties, especially for polycrystalline samples, where different distributions of grain boundaries, grains, pores, etc. can affect the electrical resistivity of the sample. Solid phase method and sol gel method are commonly used to prepare hexagonal ferrite [16]. The solid-phase preparation process is simple, but it is prone to uneven mixing for doping systems. Compared with the solid phase method, the sol gel method is a little cumbersome, but the generally synthesized samples have fine, uniform grains and high compactness, which can improve the electrical properties of the samples, especially for ferroelectric polarization measurement [17]. Therefore, BaFe_{10.2}Sc_{1.8}O_{19} samples were prepared by the sol gel method and compared with the solid phase method. Characterize the phase composition and surface morphology of the samples separately, and test the magnetic and dielectric properties of the samples.

**METHODS**

**Experimental raw materials and sample preparation**

Preparation of BaFe_{10.2}Sc_{1.8}O_{19} using solid-phase method. The raw materials are Fe_{2}O_{3}, BaCO_{3}, and Sc_{2}O_{3}, with a purity of over 99.9%. Weigh and grind three types of raw materials according to their stoichiometric ratios, and then pre-burn them for 10 hours at a temperature of 1000 ℃. After pre-firing, PVA is added, ground and pressed into sheets, and then sintered at 1250 ℃ for 32 hours to obtain the required sample.

The BaFe_{10.2}Sc_{1.8}O_{19} samples were prepared by the sol gel method. The raw materials are analytically pure Ba(NO_{3})_{2}, Fe(NO_{3})_{3}·9H_{2}O, Sc(NO_{3})_{3}·xH_{2}O, and C_{6}H_{8}O_{7}·H_{2}O. Weigh Ba(NO_{3})_{2}, Fe(NO_{3})_{3}·9H_{2}O, Sc(NO_{3})_{3}·xH_{2}O raw materials according to the stoichiometric ratio, mix and dissolve them. Weigh C_{6}H_{8}O_{7}·H_{2}O in a 1.2:1 ratio of C_{6}H_{8}O_{7}·H_{2}O to metal cations (Fe^{3+}, Ba^{2+}, Sc^{3+}). Dissolve and mix the first two, add ammonia water dropwise until neutral; then stir in an 80 ℃ water bath to gel shape, and the precursor of the sol gel method is prepared. Calcinate the precursor at 500 ℃ for 4 hours, add PVA dropwise to the calcined powder and press it into circular discs, and sinter at 1250 ℃ for 5 hours.

The surface of the wafers sintered by the solid phase method and the sol gel method were polished and polished respectively, and silver electrodes were coated on the surface of the samples to test the dielectric properties.

**Sample characterization**

Characterize the X-ray diffraction pattern (XRD) of the sample using a Japanese Science SmartLab9kW and Cu target X-ray diffractometer. Use the Quanta450FEG scanning electron microscope (SEM) produced by FEI company to observe the surface morphology of the sample, and its equipped EDS energy spectrum can analyze the distribution of elements. The magnetic and magnetic capacitance of the samples were tested using the Physical Property Measurement System (PPMS) produced by Quantum Design in the United States and the Precision Impedance Analyzer 6500B produced by WK in the United Kingdom.

**RESULTS AND ANALYSIS**

**XRD analysis**

The XRD spectra of samples obtained by different preparation methods are shown in Figure 1. (a) and (b) are the XRD spectra of samples prepared by solid phase method and sol gel method, respectively.

Comparing the XRD spectra with the PDF card (PDF # 74-1121) of the standard BaFe_{12}O_{19} spectra (the red line in the figure represents the diffraction peak position of the standard PDF card), it can be found that the XRD spectra of both samples show a significant shift to the left compared to the standard spectra. This is because the Sc^{3+} radius is larger than the Fe^{3+} radius, and the doping of Sc^{3+} increases the interplanar spacing, resulting in a shift to the left in the XRD spectra. This shows that both the solid phase method and the sol gel method have successfully made Sc^{3+} occupy the
position of Fe$^{3+}$, resulting in lattice distortion. The results indicate that all peaks that appear can be obtained by shifting the standard peak of M-phase BaFe$_{12}$O$_{19}$ to the left, and each peak position has a corresponding crystal orientation, without any impurity peaks appearing.

![X-ray diffraction pattern](image1)

**Figure 1. X-ray diffraction pattern of BaFe$_{10.2}$Sc$_{1.8}$O$_{19}$ by solid phase method and sol-gel method**

**SEM/EDS analysis**

Use SEM/EDS to characterize the surface morphology, composition, and elemental distribution of the sample. Figure 2 (a) shows the surface morphology of BaFe$_{10.2}$Sc$_{1.8}$O$_{19}$ sample prepared by solid-phase method. It can be seen that the figure is clearly divided into two parts: the dark colored part in the middle and the light-colored part on the edge. To investigate the distribution of elements, EDS was used for analysis.

![SEM and EDS analysis](image2)

**Figure 2. SEM and EDS analysis of BaFe$_{10.2}$Sc$_{1.8}$O$_{19}$ sample by solid-phase method**

Figures 2 (b), (c), and (d) show the EDS spectra of Fe, Sc, and Ba elements, respectively. It is evident that the distribution of Fe and Sc elements in the dark and light regions corresponding to Figure 2 (a) is uneven. The EDS spectra of Sc element show a significant increase in color in the
dark region of Figure 2 (a), while the color of Fe element weakens in this region. The distribution of Ba element is relatively uniform overall. The area with darker Sc element colors is defined as the "scandium rich phase", and this uneven phenomenon exists throughout the entire sample, leading to uneven distribution of elements throughout the sample. Determine the sample composition of the dark and light-colored areas in Figure 2 (a). The labeled numbers 1 and 2 in Figure 2 (a) correspond to 1 and 2 in Table 1, respectively.

Table 1. Atomic percentage of point distribution of solid-phase method samples in percent

<table>
<thead>
<tr>
<th>Element categories</th>
<th>Fe</th>
<th>Sc</th>
<th>Ba</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10.32</td>
<td>18.24</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>19.10</td>
<td>4.34</td>
<td>2.13</td>
</tr>
</tbody>
</table>

Table 1 shows the atomic percentage data of different elements at the corresponding positions of the marked points. From Table 1, it can be seen that in the first "scandium rich phase", the atomic percentage of Sc element is high, while Ba element is almost non-existent, and the content of Fe element is very low. The proportion of elements corresponding to number 2 is almost equivalent to the proportion of elements in the chemical equation BaFe_{10.2}Sc_{1.8}O_{19}, but the proportion of Sc element is still relatively high compared to the chemical formula of the sample. It is speculated that this is due to the diffusion of Sc element in the "scandium rich phase". Figure 3 (a) shows the surface morphology of the sample using the sol-gel method. It can be seen that the sample has regular hexagonal morphology, and the grains are uniform and fine, with an average grain size of 3-5 μm.

Figure 3. SEM and EDS analysis of BaFe_{10.2}Sc_{1.8}O_{19} sample by sol-gel method

Figures 3 (b), (c), and (d) show the distribution of elements corresponding to Fe^{3+}, Ba^{2+}, and Sc^{3+}, respectively. It can be seen that the color distribution is uniform, indicating that each element is evenly distributed in the sample. Table 2 shows the atomic percentage of each element in the sol-gel method sample to determine the element content distribution of the sample. The calculated element ratio is similar to that of sample BaFe_{10.2}Sc_{1.8}O_{19}, indicating that the prepared sample is an M-type hexagonal ferrite BaFe_{10.2}Sc_{1.8}O_{19}. 

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Table 2. Area distribution atom percentage of sol gel method sample in percentage

<table>
<thead>
<tr>
<th>Element</th>
<th>Fe</th>
<th>Sc</th>
<th>Ba</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic percentage</td>
<td>32.79</td>
<td>6.87</td>
<td>3.46</td>
</tr>
</tbody>
</table>

Magnetic property analysis

The magnetic properties of the samples prepared by sol-gel method and solid-phase method were studied, respectively. Figure 4 (a) shows the change curve of magnetization with temperature (MT) of the sample prepared by the sol-gel method.

It can be seen from Figure 4 (a) that there is an obvious antiferromagnetic anomaly peak at about 330 K in the curve, which indicates that the sample has a magnetic phase transition near this temperature. Tang et al., it is speculated that the corresponding phase transition point may occur in the sample from ferrous magnetic to conical magnetic structure (from high to low temperature), and this phase transition temperature is the conical magnetic structure phase transition point $T_{cone}$ of the sample [18]. Figure 4 (b) shows the MT curve of the sample prepared by the solid phase method. It can be seen that the phase transition point of the sample is about 250 K, which is very different from the result of the sample prepared by the sol gel method. It is speculated that the reason for the existence of "scandium rich phase" in the sample prepared by the solid phase method is that the Sc element actually doped into the sample is less than the theoretical value, resulting in the phase transition point not rising to the target temperature.

Figure 4. MT curve of samples by sol-gel method and solid phase method

Magnetic and dielectric effects analysis

For hexagonal ferrite, the hysteresis loop (MH curve) below the temperature range of its conical magnetic structure phase transition is quite characteristic, showing a two-step increase and then saturation behavior. Under zero magnetic field, the sample has a longitudinal conical magnetic structure. As the magnetic field intensity increases, the longitudinal conical magnetic structure tilts towards the direction perpendicular to the c-axis under the action of the magnetic field, gradually transforming into a transverse conical magnetic structure. This process is manifested in a rapid increase in magnetization intensity in the MH curve. Continuing to increase the magnetic field intensity, the cone angle of the transverse conical magnetic structure gradually decreases under the action of the magnetic field until it disappears. This is manifested in the MH curve as a slope, which has a smaller slope than the previous stag. Continuing to increase the magnetic field strength, the...
magnetic structure transforms into a sub ferromagnetic structure, and at this point, the MH curve tends to saturate. In order to further determine whether this phase transition point is the cone magnetic structure phase transition point, the MH curves above and below the phase transition point of the samples prepared by the sol-gel method were tested.

As Figure 5 (a) shows the room temperature MH curve of the sol gel method sample, it can be found that the MH curve of the sample is obviously divided into three sections: the first section is the magnetic field range of 0–0.5 T, where the number 1 is located. During this period, the magnetic moment increases rapidly with the increase of the magnetic field strength; The second paragraph covers the magnetic field range of 0.5–3T, where the number 2 is located. During this process, the magnetization intensity gradually slopes with the increase of magnetic field intensity. The third paragraph is after 3T, where the curve saturates and the number 3 is located. This behavior is the hysteresis loop behavior reflected by the conical magnetic structure, which has been reported in the research of Y-type and Z-type hexagonal ferrites [19]. According to the anti DM interaction, the transverse conical structure can generate polarization P under the action of a magnetic field, which means there is a magneto electric coupling effect at room temperature.

![Figure 5. MH curves of samples prepared by sol-gel method at different temperatures](image)

**Figure 5. MH curves of samples prepared by sol-gel method at different temperatures**

Figure 6. Room temperature MH curve of samples prepared by solid-phase method:

![Figure 6. Room temperature MH curve of samples prepared by solid-phase method](image)
Figure 5 (b) shows the MH curve of the sample obtained at 390 K, which exhibits typical soft magnetic behavior and does not exhibit segmented behavior similar to that obtained from testing at 300 K. Therefore, there is no magneto electric coupling behavior in the sample at 390 K, indicating that the phase transition point at 330 K is the cone-shaped magnetic structure phase transition point $T_{cone}$.

Compared with the MH curve of the sol gel method sample, the room temperature MH curve of the solid phase method sample (Figure 6) shows that the sample reaches saturation under a very small external magnetic field. There is no abnormal phenomenon in this process, so the solid phase method sample does not have magnetoelectric coupling behavior at room temperature. Therefore, only the magneto dielectric effect of the samples prepared by the sol gel method was tested.

It can be seen from Figure 6, at 300 K, the curves of magnetic capacitance and magnetization intensity with magnetic field variation are almost the same. Both curves gradually increasing with the increase of magnetic field intensity, and then saturating after passing through a turning point under high magnetic field, and their saturation points correspond to almost the same magnetic field size, as shown by the dashed line in Figure 5 (a). The inflection points between the two is correlated, indicating that the behavior of magnetic capacitance and magnetization intensity with the change of magnetic field is consistent. For the variation of magnetic capacitance with magnetic field, it can be understood as: in the area to the left of the dashed line, the longitudinal conical structure quickly turns to the transverse conical structure, inducing ferroelectric polarization, showing a rapid increase in magnetic capacitance. In the area between the two dashed lines, as the magnetic field strength increases, the cone angle gradually decreases, manifested as a slow increase in magnetic capacitance. In the area to the right of the dashed line, the magnetic structure transforms into a linear sub ferromagnetic structure, no longer inducing ferroelectric polarization, and the magnetic capacitance no longer changes. The ferroelectric polarization of the system can be understood through anti DM interactions. The results indicate that the conical magnetic structure can induce ferroelectric polarization.

**CONCLUSION**

The BaFe$_{10.2}$Sc$_{1.8}$O$_{19}$ samples were prepared by solid phase method and sol-gel method, respectively. The XRD analysis results indicate that all the prepared samples are pure phases. From the SEM images, it can be observed that there is an uneven phenomenon in the solid-phase method samples, namely the presence of a "scandium rich phase". The grains of the sol-gel method sample are hexagonal in shape. Compared with the solid phase method sample, the grains are significantly smaller and uniform in size. EDS analysis results show that the composition of the sol-gel method sample is evenly distributed. The change curve of the magnetization of the sol-gel method sample with temperature shows that there is a magnetic phase transition at 330 K. Combined with the previous research results and the hysteresis loop test of 300 K and 390 K samples, it is judged that this phase transition point is a conical magnetic structure phase transition point. Therefore, there is no magneto electric coupling behavior at room temperature. This research work can provide experimental basis for the preparation of excellent hexagonal ferrite, the mechanism of related magneto electric coupling, and further applications.

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**CONFLICT OF INTERESTS**

No conflict of interest.
REFERENCES


