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# Electron spin resonance (ESR) of magnetic sublattices in Sc-substituted barium hexaferrite

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The partial substitution of $Fe^{3+}$ by $Sc^{3+}$ in barium hexaferrite has shown to be an effective method to tailor anisotropy for many novel microwave applications. Some basic studies have revealed that this substitution leads to unusual interactions among the magnetic sublattices of the ferrite. In order to investigate these interactions, samples with formula $BaSc_xFe_{12-x}O_{19}$ ($1 \leq x \leq 2$) were prepared by sintering (1300°C, 6h). After structural characterization by x-ray diffraction, their ferromagnetic resonance spectra were measured in the X-band (9.4 GHz), in the 100-500 K temperature range. For $x = 2$, a single, broad resonance peak was observed at the low temperatures (103 K), exhibiting a progressive splitting into two peaks for increasing $T$, to finally coalesce again into a single (paramagnetic) narrow peak at 473 K. These results are interpreted in terms of a substitution of $Fe^{3+}$ by $Sc^{3+}$ ions in the $4f_{vi}$ and $2b$ sublattices; the diamagnetic cations disrupt the superexchange interactions and produce a splitting of the $12k$ sublattice (which interacts directly with the $4f_{vi}$ sublattice) into two sublattices with different canting angles, and different thermal dependence. As a result, the fraction of the $12k$ sublattices that are nearest neighbours of substituted $4f_{vi}$ sites can behave as an independent sublattice for some temperature ranges. A similar behavior is observed for all the compositions with varying degrees of amplitude, but it is more evident for $x = 2$. A deconvolution of peaks has been attempted, in order to shed more light into this behavior. 
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M-type hexagonal ferrites have been important materials for permanent magnet applications, and retain an important fraction of the world market. A recent review on hexagonal ferrites appeared in Ref. 1. These materials are actively investigated for novel applications, particularly for electronic devices operating at microwave frequencies.[2]

The crystal structure of M-type hexaferrites can be thought as composed of two different building blocks, R and S; the hexagonal R block contains the group $(BaFe_6O_{11})^{2-}$, and the spinel S block is formed by $(Fe_6O_8)^{2+}$. The unit cell, with two $BaFe_{12}O_{19}$ formula units, can be represented by RSR*S*, where the asterisk denotes a 180° rotation with respect to the $c$-axis. A more detailed description of the structure can be found in Ref. 3. $Fe^{3+}$ ions occupy five crystal sites, with collinear spins up and down, as shown in Table I. Ba ferrite possesses a high magneto-crystalline anisotropy (leading to an anisotropy field about 380 kA/m) and a Curie temperature of 723 K.[4]

For many novel applications, particularly in microwave devices such as filters and bandpass, it is very useful to be able to modify the anisotropy field. An effective way to do this is to produce solid solutions where iron $Fe^{3+}$ is substituted by a diamagnetic cation such as $In^{3+}$, $Ga^{3+}$, $Sc^{3+}$. This procedure allows a precise "tailoring" of magnetic properties to adapt the material to specific applications. In addition to decrease anisotropy and magnetization, these substitutions, however, have revealed unusual magnetic interactions and structures. By using a diversity of experimental methods

 

TABLE I. Magnetic sublattices in the hexaferrite structure.

| Sublattice | Symmetry | Block | spin |
|---|---|---|---|
| 12*k* | octahedral | R,S | ↑ |
| $4f_{vi}$ | octahedral | R | ↓ |
| $4f_{iv}$ | tetrahedral | S | ↓ |
| 2a | octahedral | S | ↑ |
| 2b | five-fold | R | ↑ |

such as magnetization,[5] neutron diffraction,[6,7] Mössbauer spectroscopy,[8–10] Extended X-ray Absorption of Fine Structure (EXAFS),[11] it has been found that cations ($In^{3+}$, $Ga^{3+}$, $Sc^{3+}$) have a clear preference for R-block octahedral $4f_{vi}$ and five-fold 2*b* sites. Up to $x = 2$, the substitution of non-magnetic ions on 12k sites is negligible.[8] The presence of these diamagnetic cations on $4f_{vi}$ sites disturbs the superexchange coupling with 12*k* irons and the iron spins on the 12*k* sites neighbouring Sc cations deviate from the *z*-axis. The resultant configuration exhibits a magnetic structure composed of helical blocks with different angles between adjacent blocks. These changes have been observed even for small degrees of substitution, since $4f_{vi}$ sites seem to have a critical role in the stability of the magnetic structure of the ferrite.

Recently, the combination of electrical and magnetic properties of single crystals of Sc-substituted Ba ferrite and materials of the Y-type hexagonal ferrite family ($Ba_2Mg_2Fe_{12}O_{22}$) have been investigated.[12,13] It has been confirmed that, due to the magnetic conical state, a transverse magnetic field can induce an electric polarization by the rotation of the cone axis with the application of a magnetic field. These ferrites emerge therefore as a promising multiferroic system.

In this paper, we present electron ferromagnetic and paramagnetic resonance (FMR and EPR, or more general, electron spin resonance, ESR) results on samples of the system $BaSc_xFe_{12-x}O_{19}$, with $x = 0$ to 2.0, which show evidence of two independent magnetic sublattices, particularly for $x = 2$. To our knowledge, there is only another report of these materials using ESR;[14] however, the ESR results reported are not conclusive.

Solid solution M-type $BaSc_xFe_{12-x}O_{19}$ hexagonal ferrites with $x = 0$, 0.25, 0.5, 0.75, 1.0, 1.25, 1.50, 1.75 and 2.0 were prepared by mixing $Fe_2O_3$, $BaCO_3$ and $Sc_2O_3$ in the stoichiometric proportions. After wet mixing the powders were calcined at 1300°C for 4 hours. Next the powders were wet milled with $ZrO_2$ grinding media down to a mean particle size of $d_{50} = 0.8$ μm. Pellets were fabricated by uniaxial pressing and sintered at 1370°C for 4 hours. X-ray patterns were measured with a Bruker AXS D8 Advance diffractometer using Cu $K_\alpha$ radiation. Hysteresis loops were measured at room temperature on powdered samples using a VSM magnetometer (MicroMag TM 3900, Princeton Measurements Corp., USA). Electron spin resonance (ESR) behavior of samples was obtained by means of a Magnettech Miniscope 400 spectrometer operating in the classic resonance technique, i.e., with a microwave radiation of constant frequency in the *X*-band (9.45 GHz). The applied field was swept up to 600 mT, and a dewar accessory allows measurements in the 100-500 K temperature range.

X-ray diffraction patterns for all samples showed a good agreement with the barium ferrite hexagonal structure, and no foreign diffraction peaks were detected, see Fig. 1. The *a* and *c* lattice parameters exhibited a linear dependence with composition, as shown in Fig. 2, in good agreement with Vegard's law for solid solutions. As expected, both the room-temperature coercive field and the saturation magnetization exhibited a decrease as the Sc content increases in the solid solution, as appears in Fig. 3.

The ferromagnetic resonance signals for $x = 1.50$ is shown in Fig. 4, where a complex behavior is observed. A broad signal formed by two different resonance peaks appears at 105 K. At 123 K, the low field peak increases while the high field peak decreases and practically vanishes at 273 K. However, it reappears for higher *T*. A similar behavior is observed for all the compositions with varying degrees of amplitude, but it is more evident for $x = 2$, and we will focus on this composition.

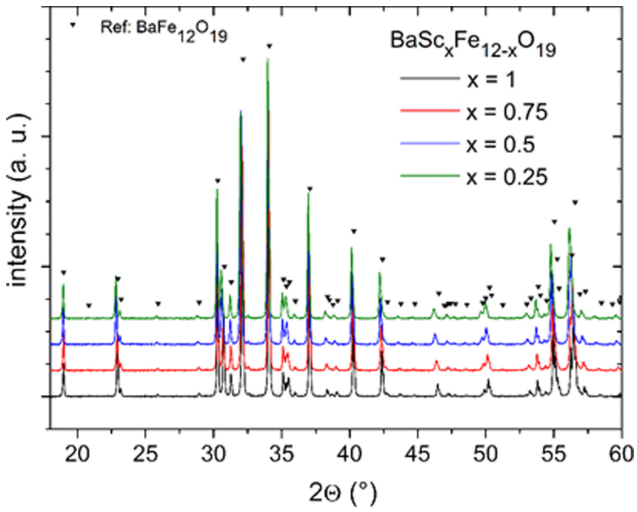


FIG. 1. X-ray diffraction patterns of samples of the $BaSc_xFe_{12-x}O_{19}$ solid solution.

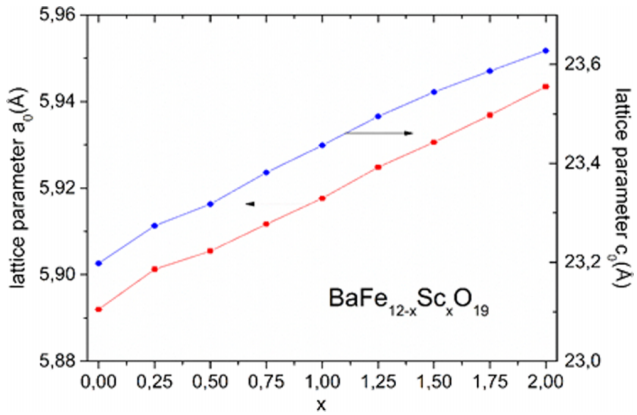


FIG. 2. Lattice parameters vs. Sc concentration for $BaSc_xFe_{12-x}O_{19}$.

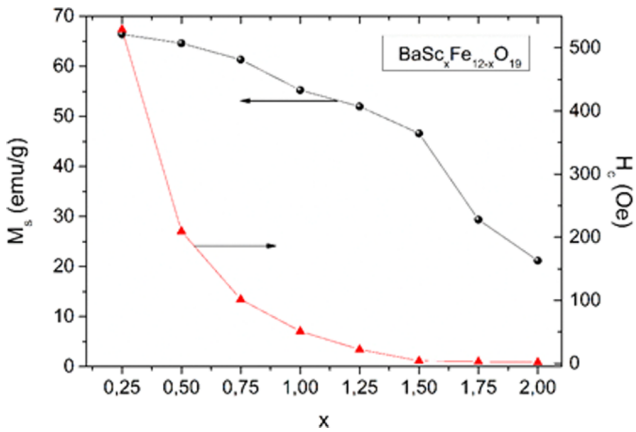


FIG. 3. Saturation magnetization and coercive field at room temperature as a function of the Sc substitution.

The low $T$ section of the resonance signals for the $x = 2$ sample is shown in Fig. 5. At 103 K, a broad resonance signal is observed. This signal is typical of an ordered ferro- or ferrimagnetic phase. As $T$ increases, this signal splits into two resonance lines which become more clearly resolved at 273 K. For higher $T$, Fig. 6, the low field signal progressively vanishes, and the high

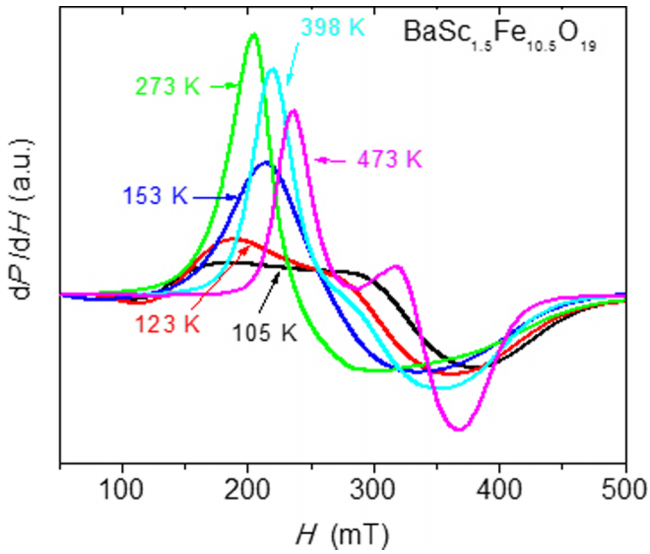


FIG. 4. Electron spin resonance of $x = 1.5$ sample as a function of temperature. The microwave frequency is 9.43 GHz.

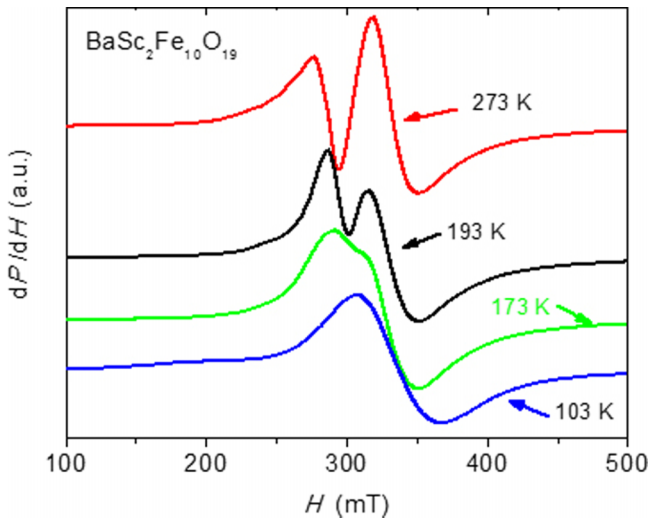


FIG. 5. ESR signals for x = 2 sample, in the low temperature range.

field signal becomes a narrow resonance line characteristic of a para-magnetic phase. The signal is symmetric and the linewidth is 15.9 mT. The resonance field for $T = 473$ K is 332.5 mT which leads to a Landé factor value $g \sim 2$, quite close to the paramagnetic spin-only value of 2.0033. The presence of a paramagnetic signal for this temperature is in good agreement with the coercive field plot (Fig. 2), where $H_C$ vanishes. The reported Curie temperature for the $x = 2$ composition is 458 K.[8]

The presence of two resonance signals in spectra is typically interpreted on the basis of two different systems of microwave absorbers; in many cases, it can be used to detect impurities, or even for magnetic field calibration when a well-known material is mixed with the phase under study. In our case, however, there is a single crystal phase, and given the previous investigations in this system, we can conclude that in the temperature ranges where two resonant signals are observed, they belong to two uncoupled magnetic sublattices: the "collinear" section which is formed by the sublattices parallel to the $z$-axis ($4f_{iv}$, $4f_{vi}$, $2a$, $2b$ and undisturbed $12k$) with the original antiparallel spins, and the "conical" sublattice, composed by the $12k$ sublattices with Sc substituted $4f_{vi}$ neighbors.

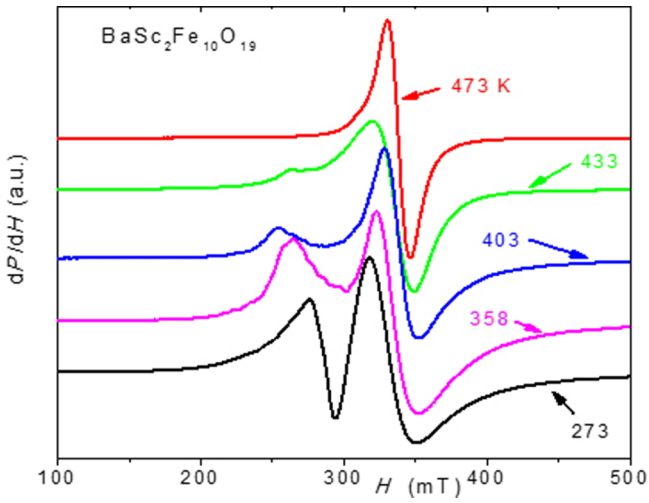


FIG. 6. ESR signals for the x = 2 sample, in the high temperature range.

For the 12*k* sublattices with broken interactions with the rest of the magnetic structure, the magnetic interactions appear stronger within these 12*k* sublattice (the "conical" ones) than with the rest of the magnetic structure. Since the 12k sublattice is the one with more magnetic cations, it can exhibit a magnetization larger than the $M_s$ typically observed close to the Curie transition. The low-field resonance peak could then be associated with the "collinear" sublattices as long as these sublattices are subjected to an internal field, while the "conical" sublattice is almost free of internal fields, and therefore is closer to a paramagnetic behavior. As can be observed in Fig. 6, as temperature increases, the high-field resonance peak is progressively transformed into the paramagnetic resonance peak with only a small increase in the applied field.

Sc-substituted solid solution $BaSc_xFe_{12-x}O_{19}$, with $x$ = 0 to 2.0, were prepared as single crystal phase and showed a systematic behavior on their unit cell parameters, magnetocrystalline anisotropy and saturation magnetization. Electron spin resonance measurements exhibited for some temperature ranges (depending on the x value) evidence of two sublattices with different resonance field, which can be attributed to the formation of two different sublattices; a collinear one (similar to the unsubstituted ferrite) and a conical one, associated with 12*k* sites. The magnetic interactions within the conical sublattice are stronger than between this sublattice and the rest of the magnetic structure, which leads to this independency of the conical sublattices. ESR appears therefore as a very sensitive method for the study of magnetic interactions.

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