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The ferromagnetic resonance (FMR) of SrZ hexaferrite ($\text{Sr}_3\text{Co}_2\text{Fe}_{24}\text{O}_{41}$), and the tuning of FMR with an external magnetic field - CI-1:IL08

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Abstract

The hexagonal Z-type ferrite $\text{Sr}_3\text{Co}_2\text{Fe}_{24}\text{O}_{41}$ (SrZ) was first synthesised in 2001 and reported as being a room temperature multiferroic material in 2010, with subsequent investigations into its multiferroic properties, but little into high frequency and microwave properties, and ferromagnetic resonance frequency (FMR), which determines its ability as an electromagnetic (EM) absorber and radar absorbing (RAM) stealth material. It was shown that SrZ existed as a majority or single phase after heating in a narrow temperature range between 1170-1190 °C using X-ray diffraction (XRD) and measurement of magnetic hysteresis loops, with the sample appearing to

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be single phase SrZ at 1190 °C. We measured complex permeability and permittivity of a single phase polycrystalline ceramic sample of SrZ between 500 MHz - 8 GHz (X-band). The sample had a relatively high permittivity >17 over this entire frequency range, and it showed a strong ferromagnetic resonance (FMR) at 2.3 GHz. This FMR could also be tuned by the effect of an external magnetic field, by moving a simple bar magnet progressively closer to a toroidal sample. This incurred a very slight shift in the peak up to 2.48 GHz at distances of 2.5-10 cm from the sample – a tuning of ~5-6% with applied magnetic fields estimated to be 0.11-0.23 T, which is not insignificant. At a close distance of 0.5 mm we got a high degree of tuning of FMR to 3.4 GHz, a large change of 1.07 GHz (= 46% increase) with an applied magnetic field estimated to be 0.40 T. Despite this, the applied field had no significant effect on permittivity over 0.5-8 GHz. Such results have never been reported before, and are significant, as this would enable tuning of the FMR via simple physical/mechanical movement of a bulk alloy magnet, effectively creating a tuneable microwave filter or absorber.

1. Introduction

The hexagonal ferrites have been greatly important materials commercially and technologically since their discovery in the late 1950's, used as permanent magnets, as well as magnetic recording and data storage materials, components in electrical devices operating at microwave / GHz frequencies for mobile and wireless communications, and as electromagnetic (EM) wave absorbers for electromagnetic compatibility (EMC) testing, EM shielding and radar absorbing materials (RAM) and stealth technologies.¹ One of the most exciting recent developments has been the discovery that $\text{Sr}_3\text{Co}_2\text{Fe}_{24}\text{O}_{41}$ Z-type hexaferrite (SrZ) is a single phase magnetoelectric / multiferroic material at room temperature.²

Philips Laboratories developed the hexagonal ferrites in the 1950's from the BaO-Fe₂O₃ system, initially with BaFe₁₂O₁₉ (M ferrite, BaM),³ and then producing more complex hexagonal compounds in the ternary BaO-Fe₂O₃-MeO system (Me = a small divalent cation).^{4,5} Many hexaferrites have a preferred direction of magnetisation giving them uniaxial magnetocrystalline anisotropy, making these magnetically hard ferrites with high coercivity (H_c). However, some compounds containing a divalent cation, such as cobalt, have a plane (or cone) of spontaneous magnetisation in the basal plane, perpendicular to the *c*-axis, which can easily rotate within the plane through an angle of 360°, making them soft ferrites (low H_c). These are known as hexaplana ferrites, and the Z ferrites are in this class.^{1,4,5} Single phase barium Z ferrite is complex to produce, because the structure of Z is a combination of M ferrite and Y ferrite (Ba₂Me₂Fe₁₂O₂₂), and it has been found that Ba₃Co₂Fe₂₄O₄₁ (Co₂Z) never forms directly, but always results from the topotactic reaction of the two previously formed M and Y stages (formed at around 1000 °C), irrespective of the starting materials.⁶ As the Co₂Z phase forms at around 1250 °C⁷ discontinuous grain growth (DGG) also typically occurs, giving a large platy grain structure,⁸ and Co₂Z is stable up to 1300 °C, experiencing even greater DGG at high temperatures.⁹

Barium can be fully substituted by strontium in the Z structure, and Sr₃Zn₂Fe₂₄O₄₁ Z-ferrite was reported in 1970.¹⁰ Sr₃Co₂Fe₂₄O₄₁ (SrZ) was first synthesised by Pullar and Bhattacharya from an inorganic sol-gel precursor in 2001, forming the single Z phase at 1200 °C from SrM (SrFe₁₂O₁₉), α-Fe₂O₃ and CoFe₂O₄ phases,¹¹ *without* prior formation of the Y phase as an intermediate, a feature that has

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2 always been observed as a co-precursor in the formation of barium Z ferrites, and
3 without DGG. Since then a series of Sr-substituted $(\text{Ba}_{1-x}\text{Sr}_x)_3\text{Co}_2\text{Z}$ was made with $x =$
4 $0-0.8$ at $1250\text{ }^\circ\text{C}$,¹² polycrystalline $\text{Ba}_{1.5}\text{Sr}_{1.5}\text{Co}_2\text{Z}$ and $\text{Sr}_3\text{Co}_2\text{Z}$ from were made from
5 stoichiometric oxides/carbonates by solid state methods and heated to 1250 and 1210
6 $^\circ\text{C}$ to give well-sintered samples,¹³ and it has often been shown that single phase
7 $\text{Sr}_3\text{Co}_2\text{Z}$ has a very small thermal stability range between around $1180-1210\text{ }^\circ\text{C}$ – for
8 example, single phase SrZ was demonstrated to exist between $1195-1210\text{ }^\circ\text{C}$, but
9 contained other phases at $1190\text{ }^\circ\text{C}$ and $1220\text{ }^\circ\text{C}$.¹⁴

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15 SrZ was first reported by Pullar and Bhattacharya¹¹ as having a saturation
16 magnetisation (M_s) of $48.5\text{ A m}^2\text{ kg}^{-1}$, and was a very soft ferrite with $H_c = 5.6\text{ kA m}^{-1}$
17 - it has since been shown that SrZ is a hexaplana ferrite at RT, with a cone of
18 magnetisation at an angle of 52.3° to the c-axis.¹⁵ Pullar and Bhattacharya also
19 reported a curious and drastic change in shape of the hysteresis loop at an applied
20 field of 1.5 T , and although they could not explain this two-step magnetic process
21 observed in a single phase ferrite, they made a reference to the non-collinear structure
22 seen in $\text{Sr}_2\text{Zn}_2\text{Y}$,¹⁰ which had a similarly shaped loop. However, it was this report that
23 drew the attention of Kitagawa *et al.*¹⁶ to SrZ as a potential magnetoelectric ferrite, as
24 it appears that this step wise change in M_s with applied magnetic field in a pure phase
25 hexaplana ferrite can be an indication of possible non-collinear magnetic structures,
26 with potential as magnetoelectric/multiferroic ferrites. This two-step loop shape can
27 also be used as a means to conform the formation of pure phase/ near pure phase SrZ ,
28 as the other phases with which it may coexist (e.g. $\text{SrFe}_{12}\text{O}_{19}$ (SrM), $\text{SrCo}_2\text{Fe}_{16}\text{O}_{27}$
29 (SrW), are not non-collinear in nature.

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Despite the great interest in SrZ as a single phase room temperature
magnetoelectric/multiferroic material, there are few detailed investigations into its
high frequency properties. This is surprising, as it is well established that Co_2Z , the
barium analogue, is a good microwave absorber at useful frequencies in the low GHz
range, with ferromagnetic resonance (FMR) at 1.3 GHz .^{17, 18} High frequency
measurements carried out on SrZ in 2012, heated to between $1160-1200\text{ }^\circ\text{C}$ as a
sintered toroid and looking at the effects of applied voltage on complex permeability
at up to 4 GHz , showed a broad, poorly defined FMR peak between about $2.5-3.5$
 GHz ,¹⁹ and a magnetic permeability μ of $3-4$ over $0.5-4\text{ GHz}$. The authors of this
paper presented the FMR frequency of SrZ of a toroid sintered at $1190\text{ }^\circ\text{C}$ as being 2.3

1 GHz at the Microwave Materials and their Applications conference in 2016
2 (MMA2016, no published article),²⁰ and a broad FMR around 2.5 GHz in SrZ made
3 by the solid state route, heated to 1210 °C and measured as a composite of 10% SrZ in
4 epoxy polymer ($\mu \sim 3$) was reported in 2019.²¹ Since then it has also been reported as
5 being between 2.9-3.3 GHz in samples made by citrate sol-gel (with $\mu = 3-6$),
6 although these were heated to unusually high temperatures of 1195-1245 °C to form
7 the SrZ phase and measured as composites of 10% SrZ in an epoxy polymer, and did
8 not exhibit strongly two-phase hysteresis loops.²²

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11 In this this paper, we investigate the complex permeability, permittivity and FMR
12 frequency of SrZ between 1-8 GHz. We also look at the effect of tuning FMR by
13 applying an external magnetic field using a simple permanent bar magnet, i.e. not an
14 applied EM field from a coil with a current passing through it, which could also have
15 unwanted magnetoelectric effects.

16 17 18 19 20 21 22 23 24 25 26 27 **2. Experimental**

28 29 30 *2.1 Synthesis of Sr₃Co₂Fe₂₄O₄₁ (SrZ) powders*

31 Stoichiometric amounts of SrCO₃ (99% Sigma-Aldrich), Co₃O₄ (99% Sigma-Aldrich)
32 and Fe₂O₃ (99% Prolabo) were well mixed and calcined at 1000 °C / 16h, after which
33 the powder was ball milled in propan-2-ol to reduce agglomeration and particle size.
34 This was then heated to 1150, 1170 and 1190 °C / 3 hr in air to produce SrZ powders,
35 which were again ball milled as above.

36 37 38 39 40 41 42 *2.2 Synthesis of SrZ toroids*

43 The powder heated to 1190 °C was used to to form the toroids (7 mm diameter, 3.5
44 mm height, 3 mm hole in the centre) used for microwave/GHz measurements, pressed
45 from a die and sintered at 1190 °C for 3 h in air.

46 47 48 49 50 51 52 *2.3 XRD measurements*

53 The samples heated to 1150-1190 °C were analysed by XRD using a PANalytical
54 X'PERT PRO 3 instrument (Cu-K α radiation, $2\theta = 20-70^\circ$, 0.01° step scan and 200
55 s/step). Phase identification was made using HighScore Plus software, and JCPDF
56 standard patterns.

2.4 Magnetic measurements

Magnetic measurements were performed using a commercial vibrating sample magnetometer (VSM) with a maximum applied magnetic field of 3 T, at room temperature, on the powders heated to 1150, 1170 and 1190 °C.

2.5 Complex permeability and permittivity and magnetic tuning measurements

For frequency domain characterisation of the magnetic permeability and the complex electrical permittivity, transmission and reception (T/R) measurements were used in an air transmission line of a two-port system,²³ where complex magnetic permeability and electrical permittivity were determined over a frequency range from transmission and reflection coefficients measured with an Agilent Model 8722ES Vector Network Analyzer (VNA) as shown in figure 1.

Samples with toroidal geometry were inserted between the inner and outer conductors of the coaxial line with terminations coupled to a sample port model APC-7 with characteristic impedance of 50 Ω , compatible with the input impedance of the VNA. After being calibrated in the desired frequency range with a VSWR value (voltage standing wave ratio) close to 1, measurements of the scattering parameters (S parameters) were carried out whose data were sent to a computational platform where an NRW conversion algorithm (Nicolson -Ross-Weir^{24,25}) allows the direct conversion of the complex measurements of magnetic permeability (μ^*) and electrical permittivity (ϵ^*) of the investigated composition through a computational routine carried out in the Agilent VEE Pro 9.3 environment, implemented taking into account the theoretical concepts associated with the material studied and the uncertainties in measurements caused by geometric imperfections in the sample.²⁶

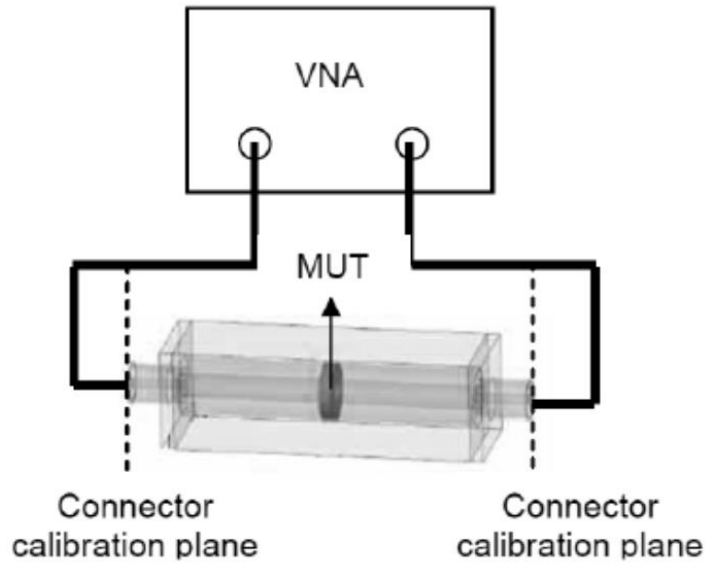


Fig. 1 The measurement set-up used for complex permeability and permittivity measurements (VNA = vector network analyser, MUT = material under test).

3. Results and discussion

The XRD results for the powders heated to 1150, 1170 and 1190 °C are shown in Fig.2. The powder heated to 1150 °C was shown to be a mixture of α -Fe₂O₃, SrM and SrZ (as a minority phase), with probably some CoFe₂O₄ present as well (Fig. 2a). When heated to 1170 °C, the sample was mostly SrZ, but with some SrM, and possibly CoFe₂O₄, still present (Fig. 2b). As is usual with the formation of SrZ, no evidence of a Y-ferrite phase (e.g., Sr₂Co₂Fe₁₂O₂₂) was observed, unlike in the formation of barium Co₂Z ferrite. After heating to 1190 °C, the sample was clearly virtually all, if not completely, SrZ (Fig. 2c). When heated too much, the SrZ phase decomposes in to the SrW phase (SrCo₂Fe₁₆O₂₇), and these phases can be very difficult to tell apart. Therefore, we show a smaller section of the XRD pattern for the sample at 1190 °C (Fig. 2d), with the peak positions for SrZ and SrW marked by blue dotted and red dashed lines, respectively. We have also added a standard pattern representing the XRD data given by Kikuchi *et al.* (in green),¹⁴ which is different from the standard pattern 04-019-4353 in several aspects, in particular the peaks at around 24° (present in our sample) and around 34° (absent in our sample) not present in the standard, and the small shift in position of several other peaks. Although some W ferrite peaks overlap with, or are very close to, the Z ferrite peak, there is no clear

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indication of the presence of a SrW phase. We feel that this is evidence that we have a single phase SrZ sample after heating to 1190 °C.

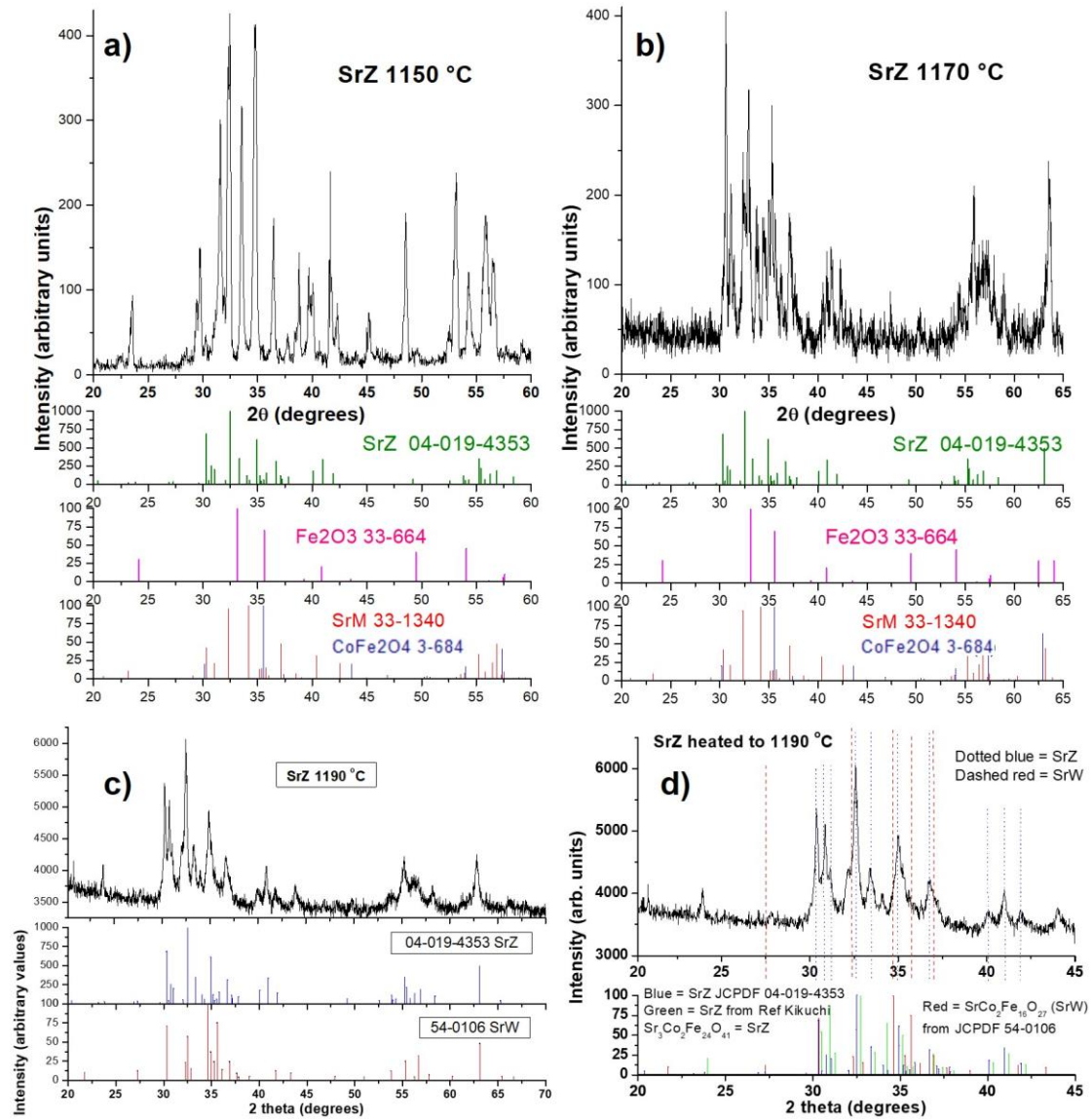


Fig. 2 XRD patterns of SrZ powders heated to a) 1150 °C, b) 1170 °C and c) 1190 °C. Peak positions shown for standards for SrZ (blue dotted lines) and SrW (red dashed lines) on a section of the pattern for the 1190 °C sample in d).

This was further confirmed by the room temperature magnetic hysteresis loop measurements, as shown in Fig. 3. All three samples showed the two stage hysteresis loop typical of the non-collinear magnetic structure of SrZ, indicating that there was

indeed a significant of SrZ present even at 1150 °C, along with SrM (and possibly some CoFe_2O_4) and the nonmagnetic $\alpha\text{-Fe}_2\text{O}_3$. However, the two step loop is much better defined in the sample heated to 1170 °C (nearly single phase SrZ), and even more so for that heated to 1190 °C (single phase SrZ). The magnetisation values are around $50 \text{ A m}^2 \text{ kg}^{-1}$ ($= 50 \text{ emu g}^{-1}$), which is the expected value for SrZ ferrite. SrM has a higher magnetisation of around $60 \text{ A m}^2 \text{ kg}^{-1}$,¹ but that will have been offset in the sample heated to 1150 °C by the presence of nonmagnetic $\alpha\text{-Fe}_2\text{O}_3$. All of the samples are extremely soft ferrites, with a coercivity (H_c) approaching zero, which is to be expected for SrZ ferrite, but this is a surprise in the sample heated to 1150 °C which appears to contain a significant amount of SrM, a hard ferrite with high H_c . The sample heated to 1190 °C had a magnetisation of $51.6 \text{ A m}^2 \text{ kg}^{-1}$ at 3 T (which will be very close to its saturation magnetisation, M_s), a very low remnant magnetisation (M_r) of $2.9 \text{ A m}^2 \text{ kg}^{-1}$ at 0 T, and H_c was only $1.5 \times 10^{-4} \text{ T} = 1.5 \text{ Oe} = 120 \text{ A m}^{-1}$. This confirms that this sample is single phase SrZ.

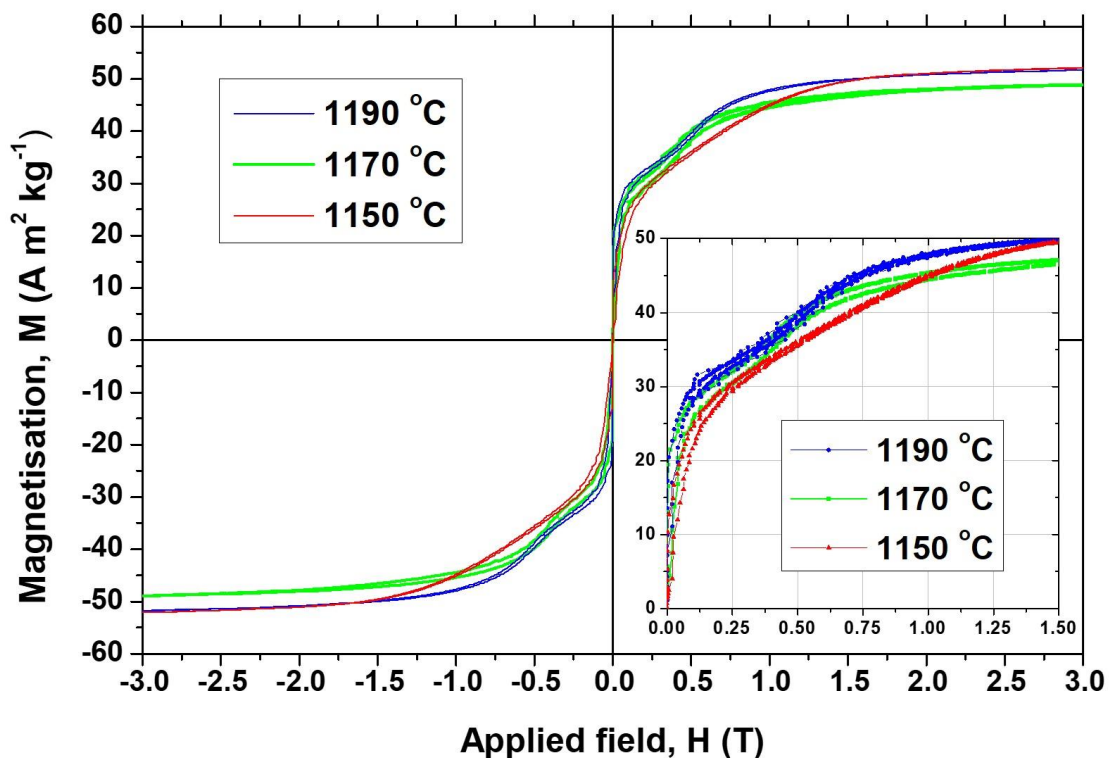
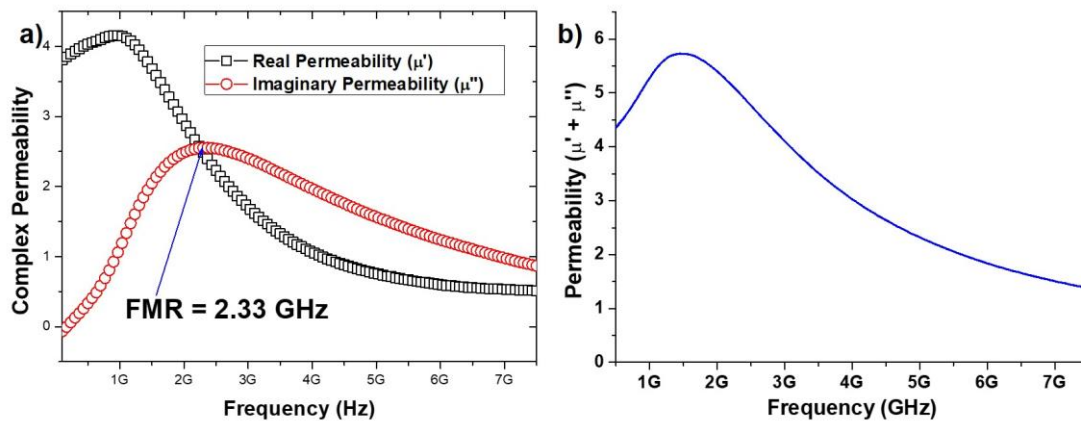


Fig. 3 Magnetic hysteresis loops for the SrZ powders heated to 1150, 1170 and 1190 °C.

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 2 The complex permeability measured for the toroid sintered from the pure SrZ
 3 powder heated to 1190 °C is shown in Fig. 4a. The FMR can be seen when there is a
 4 peak in the imaginary permeability (μ'') coincident with a 50% decrease in the real
 5 permeability (μ'). This occurs at a frequency of 2.33 GHz for the SrZ toroid, which is
 6 significantly higher than that observed in Co₂Z ferrite (Ba₃Co₂Fe₂₄O₄₁), which has an
 7 FMR frequency of 1.3 GHz.^{17,18} This agrees with the values reported by Park and
 8 Kang for SrZ heated to 1210 °C,²¹ but is lower than the values of 3-3.5 GHz reported
 9 by Ebnabbasi *et al.*¹⁹ on a toroid sintered between 1160-1200 °C and annealed in
 10 oxygen at 600 °C, and 3-3.3 GHz by Heo *et al.* for SrZ heated to 1195-1245 °C and
 11 measured as a 10% composite sample in epoxy polymer.²² The magnetic permeability
 12 ($\mu' + \mu''$) peaks at around 6 at 1.45 GHz (Fig. 4b), dropping to around 2 at 7 GHz,
 13 and with a value of 5 at the FMR frequency of 2.33 GHz. This is similar to values reported
 14 for Co₂Z ferrite, and those reported for SrZ by Heo *et al.*,²² and higher than that
 15 reported by and Ebnabbasi *et al.*¹⁹ (around 4), but lower than that observed by Park
 16 and Kang (around 7.5).²¹ Nevertheless, this is sufficient for use as a microwave
 17 absorbing or RAM material, and the broadness of the FMR is also useful in this
 18 aspect.
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52 Fig. 4 a) Complex permeability (real permeability μ' and imaginary permeability
 53 μ'') and FMR of SrZ toroid sintered from powder heated to 1190 °C. b) Change in
 54 magnetic permeability μ between 0.5-7.5 GHz.
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The complex permittivity (real permeability (ϵ') and imaginary permeability (ϵ'')) is shown in figure 5a. There was generally little change between 1-7.5 GHz, although some minor dielectric resonances were observed. There were broad resonances centred around 1.7 GHz and 2.85 GHz, and several very small resonances between 3.15-3.37 GHz. The permittivity (dielectric constant ϵ , a measure of the degree of electrical polarisation) was >17 over the entire 1-7.5 GHz range (Fig. 5b), surprisingly high for a hexaferrite, as these materials always contain small amounts of Fe^{2+} , increasing their electrical conductivity. This is considerably higher than the values <10 reported by Heo *et al.* between 100 MHz-10 GHz,²² and similar values from Park and Kang in the GHz region.²¹

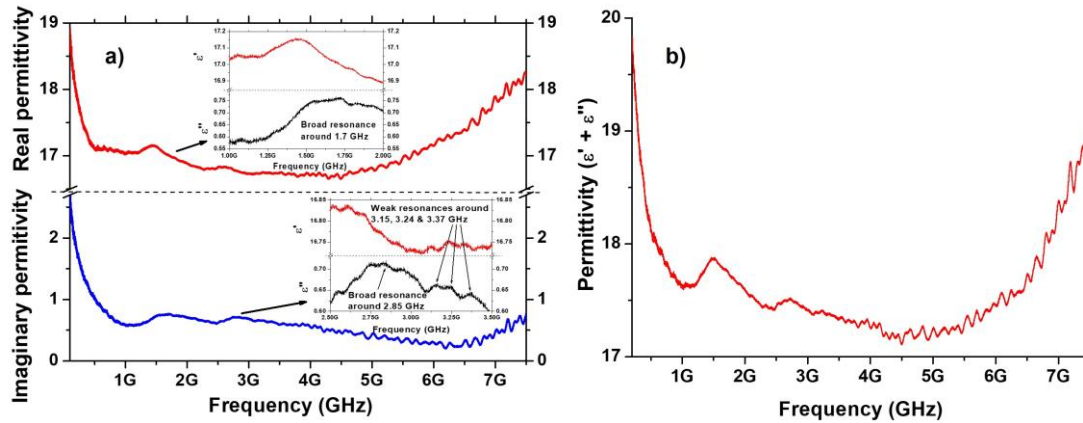


Fig. 5 a) Complex permittivity (real permittivity ϵ' and imaginary permittivity ϵ'') of SrZ toroid sintered from powder heated to 1190 °C. Minor dielectric resonances are indicated in the inserts. b) Change in permittivity ϵ between 0.1-7.5 GHz.

The magnetic tuning experiments were carried out by placing an alloy permanent bar magnet a varying distance from the measurement cavity, which contained the SrZ as a sintered toroid made from the powder heated to 1190 °C. The experimental set-up is depicted in Fig. 6a. As the bar magnetic was moved from 25 mm away (at which distance no effect on FMR was observed) to be closer to the sample, initially a small but gradual change in the real and imaginary permeability was observed, for distances of 10-2.5 mm from the sample (Fig. 6b). However, when the magnet was 0.5 mm from the measurement cavity, a large change in the complex permeability occurred.

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The real and imaginary permeability peaks moved to higher frequencies, became broader, and the values of both also decreased. The shift in FMR with magnet distance is shown in Fig. 6c, and while for distances of 10-2.5 mm there was only a small increase in FMR frequency, from 2.33 GHz to around 2.45 GHz (~5-6% increase), when the magnet was only 0.5 mm from the cavity there was a large increase to 3.40 GHz (45.9% increase). The FMR peak also became significantly broader. The FMR peak was at 2.44, 2.45 and 2.48 GHz for distances of 10, 5 and 2.5 mm from the measurement cavity, respectively, giving increases in FMR of 4.7%, 5.2% and 6.4%, respectively. The change in magnetic permeability μ is shown in Fig. 6d, and it can be seen that as the magnet moved closer to the SrZ, there was a reduction in permeability around the peak in μ (from nearly 6 to 4) and at lower frequencies, although there is no change at frequencies greater than 4 GHz. The frequency at which the peak value in μ occurred also increased as the magnetic neared the sample.

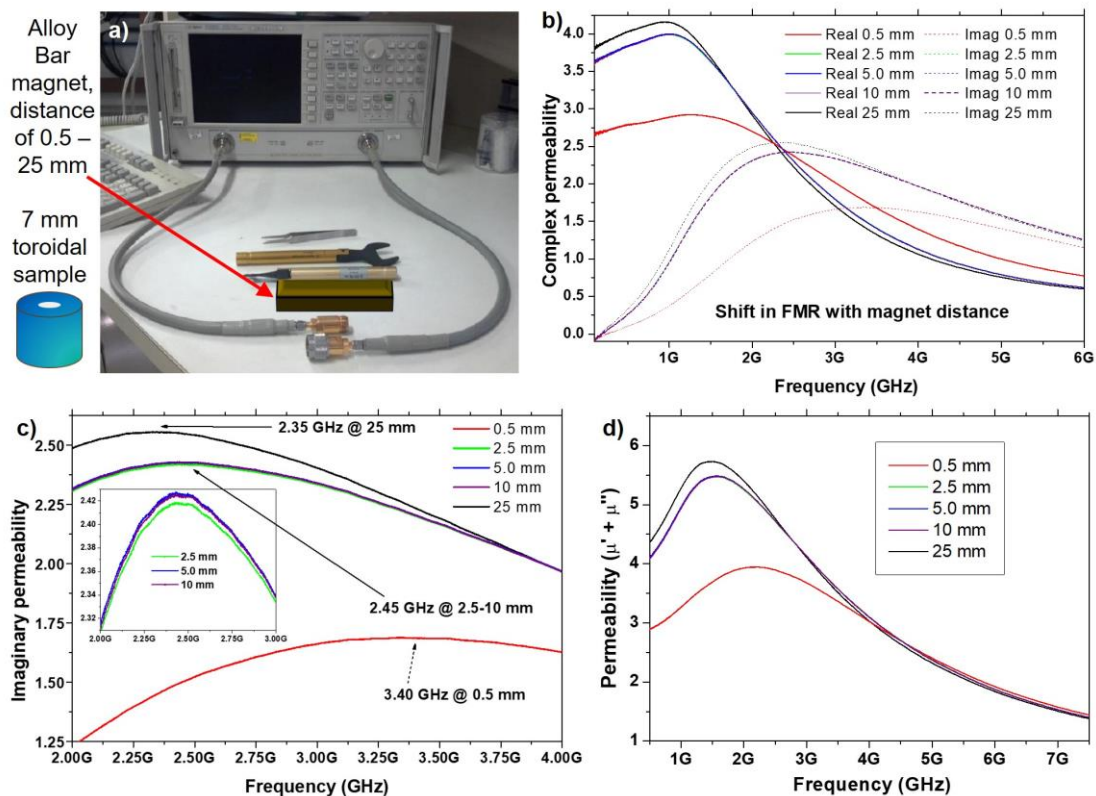


Fig. 6 Magnetic tuning of the FMR and permeability. a) the experimental set up with a permanent alloy bar magnet placed between 0.5-25 mm away from the measurement cavity, which contains a 7 mm diameter toroidal SrZ sample. b) Change in complex permeability with magnet distance from the measurement cavity. c) The

1 shift in FMR frequency with magnetic distance from the measurement cavity. d)
2 Variation in magnetic permeability μ with magnet distance from the measurement
3 cavity.
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8 There was no change in the frequencies of the small dielectric resonances as the
9 magnet was moved closer (Fig. 7a), and little variation in the permittivity (dielectric
10 constant ϵ) which remained at around 17 or greater in all cases. In hexaplana ferrites
11 with planar (or in-cone) anisotropy the natural FMR frequency will be governed by
12 the rotational stiffness of the magnetisation within the ab plane as well as the stiffness
13 out of the ab plane, and the gyromagnetic ratio (ratio of the magnetic moment to the
14 angular momentum).¹⁸ Therefore, although the FMR frequency had been affected by
15 the effect of the external magnetic field on the rotation of the magnetisation, it had
16 virtually no effect on electrical polarisation of the ferrite, despite the likelihood of
17 some magnetostriction occurring.
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27 In order to estimate the strength of the applied magnetic field, the magnetic field
28 of the bar magnet was measured at various distances. At the surface it had a field of
29 0.46 T, and this was also measured at distances of 5, 10, 15, 20 and 25 mm from the
30 magnet, as shown in Fig. 7b. At a distance of 25 mm no measurable field ($<0.001\text{T}$)
31 was detected, and indeed the magnet had no effect on μ or FMR frequency when
32 placed this distance. The plot of the log of the magnetic field B with distance is shown
33 in the inset of Fig. 7b, and this gives a linear relationship, as expected. This then
34 allowed us to extrapolate and estimate the magnetic field applied by the bar magnet at
35 the distances used during the experiments, as shown in Fig. 7c. The applied field was
36 0 T at a distance of 25 mm from the cavity, 0.03 T when at 10 mm, 0.11 T at 5 mm,
37 0.23 T at 2.5 mm and 0.40 T at 0.5 mm. The variation in FMR frequency with applied
38 external field is shown in Fig. 7d.
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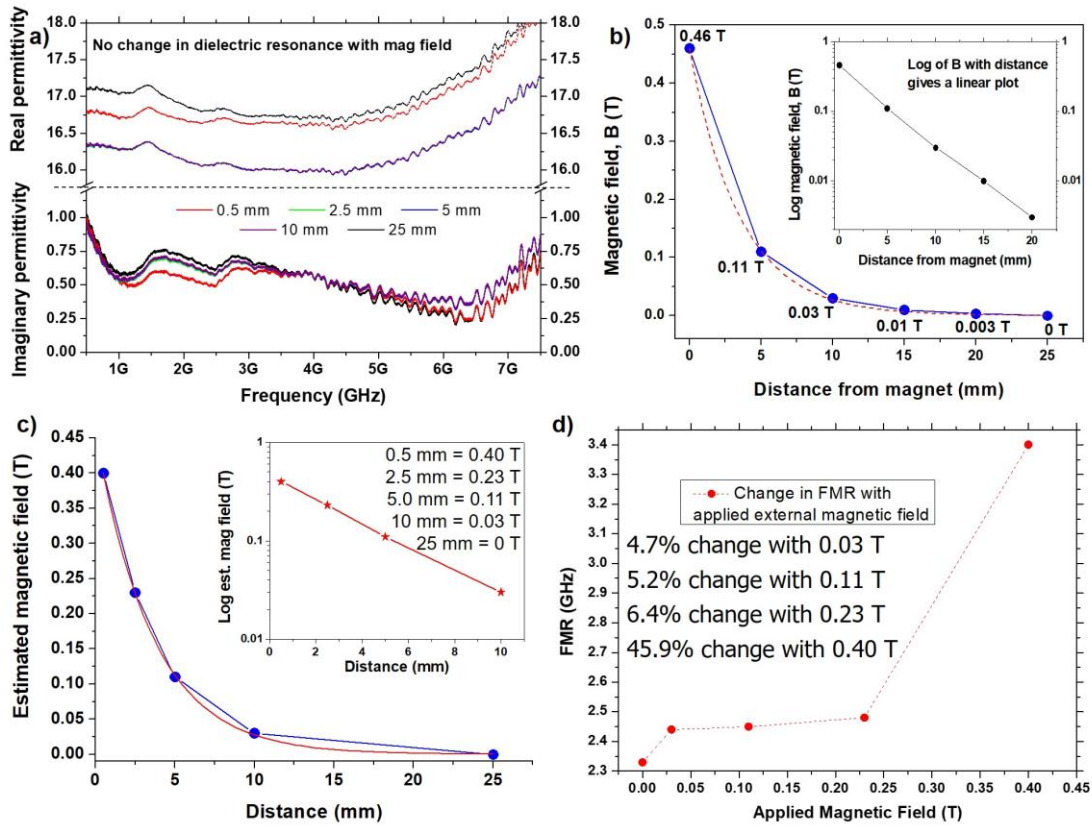


Fig. 7 a) Effect of magnet distance from the measurement cavity on the complex permittivity. b) Measurement of the magnetic field at various distances from the bar magnet. c) Estimate of the applied magnetic field during magnetic tuning experiments for various distances from the measurement cavity. d) Change in FMR frequency with magnitude of the applied external magnetic field.

The effects of the applied external magnetic field are extremely non-linear, with little change for fields up to 0.23 T (6% change), but then a very large degree of tuning (46%) with a field approximately double that, of 0.4T. This suggests that there may be a critical magnetic field strength, between these two values, possibly at which the degree of magnetostriction incurred has a major effect on the in-plane rotational stiffness, and hence the FMR of the ferrite. The fact that there is little effect on the dielectric properties suggests that there is no significant change in the electrical polarisation of the ferrite despite this.

4. Conclusions

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It was confirmed that there exists a very narrow temperature range for the formation of $\text{Sr}_3\text{Co}_2\text{Fe}_{24}\text{O}_{41}$ Z ferrite, with a nearly single phase sample forming at 1170 °C, and a single phase sample being formed at 1190 °C. This had the typical two-step magnetic hysteresis loop showing the non-collinear nature, and was an extremely soft ferrite, with M_s of 51.6 A m² kg⁻¹, a small M_r of 2.9 A m² kg⁻¹, and H_c of only 120 A m⁻¹ (1.5 Oe). The complex permeability and permittivity were measured at microwave frequencies between 0.5-8 GHz (X band). A broad FMR was shown to occur at 2.33 GHz, with a magnetic permeability μ of 5 at this frequency. There were several minor dielectric resonances between 1.7-3.4 GHz, and the sample had a relatively high permittivity $\epsilon > 17$ over the entire frequency range measured.

Tuning of the FMR frequency was achieved by moving an alloy permanent bar magnet between 0.5-25 mm from the measurement cavity, and an increase of the FMR frequency of up to 46% (to 3.40 GHz) was achieved with an applied external field of 0.4 T. The non-linear nature of the increase in FMR frequency with applied magnetic field suggest that there may be a critical field value beyond which major changes in the in-plane rotational stiffness can be incurred. The applied external magnetic field had little effect on the complex permittivity or electrical polarisation of the ferrite. These results show that the construction of a simple GHz filter or variable RAM or EM shielding device, modulated by the mechanical positioning of a bar magnet in the vicinity of the hexaferrite would be possible, in which, for instance, a stepper motor or grub screw could be used to accurately change the distance, and hence tune the FMR. This raises the possibility of affordable and simple mechanically tuneable FMR devices.

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