Synthesis, Characterization, and Electromagnetic Wave Absorbing Properties of $M_1^{2+}$–$M_2^{4+}$ Substituted M-Type Sr-Hexaferrites

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Abstract: Mn–Ti, Zn–Ti, Zn–Zr substituted M-type Sr-hexaferrites (SrM), $\text{SrFe}_{12−2x}\text{M}_1\text{M}_2\text{O}_{19}$ ($0 \leq x \leq 2.0$, $M_1 = \text{Mn or Zn}$, $M_2 = \text{Ti or Zr}$) were synthesized, and their solubility, crystalline structure, and high-frequency properties were studied. Zn–Zr substitution caused a relatively large lattice parameter change and resulted in lower solubility ($x \leq 1.0$) in the M-type phase compared with Mn–Ti and Zn–Ti substitutions. However, the ferromagnetic resonance frequency ($f_{\text{FMR}}$) effectively decreased with increasing $x$ in $\text{SrFe}_{12−2x}\text{Zn}_x\text{Zr}_x\text{O}_{19}$ (Zn–Zr: SrM) ($0 \leq x \leq 1.0$) and the electromagnetic wave (EM) absorption frequency also varied according to the shift in $f_{\text{FMR}}$ in the 7–18 GHz range. This is attributed to a gradual decrease in the magnetocrystalline anisotropy of Zn–Zr: SrM ($0 \leq x \leq 1.0$) with an increase in $x$. Zn–Zr: SrM ($x = 0.9$)–epoxy (10 wt%) composites exhibited a high EM absorption in the X-band (8–12 GHz) with the lowest reflection loss of $<-45$ dB. The sample with $x = 0.8$ showed a broad Ku band (12–18 GHz) absorption performance satisfying RL $<-19$ dB at $11 \leq f \leq 18$ GHz.

Keywords: hexaferrite; permittivity; permeability; ferromagnetic resonance; reflection loss; EM absorption

1. Introduction

Hexaferrite materials have attracted significant research interest in the past several decades owing to their interesting physical properties, such as their hard magnetic, magnetoelectric, electromagnetic absorption and magneto-dielectric properties. M-type Sr hexaferrites SrFe$_{12}$O$_{19}$ (SrM) are well-known hard magnetic materials used in permanent magnets because of their favorable hard magnetic properties, excellent phase stability, and low material cost [1,2]. The magnetic properties of SrM can be altered to become either harder or softer through cation substitutions. It has been reported that cation co-substitution of La–Co or La–Ca–Co into SrM increase the magnetocrystalline anisotropy [3,4], resulting in an enhancement of the permanent magnet performance, while, in contrast, those of Co$^{2+}$–Ti$^{4+}$ [5–7], Ti$^{2+}$–Mn$^{4+}$ [8–10], Mn$^{2+}$–Zr$^{4+}$ [11], and Mn$^{4+}$–Zn$^{2+}$ [12] result in a decrease in magnetocrystalline anisotropy. Cation-substituted SrM is also a promising candidate for high-frequency soft magnetic devices such EM wave absorbers [6,10–15].

When EM waves are irradiated into a material, the interactions of absorption, reflection, and transmission are classified based on the complex permittivity $\varepsilon = \varepsilon' - j\varepsilon''$ and permeability, $\mu = \mu' - j\mu''$ of the material. The imaginary parts of the permittivity ($\varepsilon''$) and permeability ($\mu''$) are closely related to EM absorbing performances through the dielectric or magnetic loss mechanism, respectively. In addition, good impedance matching characteristics that are functions of these $\varepsilon'$, $\varepsilon''$, $\mu'$, and $\mu''$ material parameters are also important for the high EM absorbing performances without high EM reflection [16]. Recently, improved EM absorbing or shielding properties at GHz range have been reported by designing the nanocomposites where EM active materials are employed in template
materials [17–19]. In the research, high EM absorbing performances with a relatively broad absorption bandwidth could be achieved through controlling the composite structures and its complex permittivity and permeability properties. The EM wave absorption of insulating hexaferrites is mostly dependent on the magnetic loss mechanism, which is closely related to the imaginary part of the permeability ($\mu''$). The $\mu''$ of hexaferrites increases at the ferromagnetic resonance (FMR) frequency ($f_{FMR}$), which is related to the magnetic anisotropy field ($H_{ani}$) by the equation below [20], where $\gamma$ is the gyromagnetic ratio and $\mu_0$ is the permeability of vacuum.

$$f_{FMR} = \frac{\gamma \mu_0}{2\pi H_{ani}}$$

SrM has a high $f_{FMR}$ of ~50 GHz, which is too high for hexaferrites to function as EM absorbers in the commercial radar frequency range, such as the X-band (8–12 GHz) and Ku-band (12–18 GHz). It has been reported that Co–Ti co-substitution effectively decreases the $f_{FMR}$ from 50 to a few gigahertz for a substitution $x$ range of $0 \leq x \leq 1.5$ for SrFe$_{12-2x}$Co$_x$Ti$_x$O$_{19}$ [5]. In our previous research [7], the EM absorption properties of Co–Ti-substituted Sr-hexaferrites ($1.1 \leq x \leq 1.3$) changed gradually from 6 to 15 GHz, which included the X-band (8–12 GHz) of interest in terms of radar applications. It was demonstrated that the EM absorption area can vary according to the gradual shift of the $f_{FMR}$. As cobalt is an expensive element, it is important to find other substitution elements that are more price competitive. The EM absorption properties of Ti–Mn [8–10] and Mn–Zr [11] substituted M-type hexaferrites have been reported. However, systematic studies with varying substitution amounts and correlations among composition, magnetic properties, and EM absorption properties are rare. In particular, to the best of our knowledge, the EM absorption properties of Zn–Zr substituted M-type hexaferrites have not yet been reported. In this study, Zn–Ti, Mn–Ti, and Zn–Zr co-substituted SrM with the chemical formula SrFe$_{12-2x}$M$_1$xM$_2$xO$_{19}$ ($0 \leq x \leq 2.0$, $M_1 = \text{Mn or Zn}; M_2 = \text{Ti or Zr}$) were synthesized, and their crystalline structures, microstructures, high-frequency permeability, permittivity, and EM absorption properties were systematically studied.

2. Materials and Methods

M-type hexaferrites with chemical formulae of SrFe$_{12-2x}$Zn$_x$Ti$_x$O$_{19}$, SrFe$_{12-2x}$Mn$_x$Ti$_x$O$_{19}$ ($x = 0, 0.5, 1.0, 1.5, 2.0$), and SrFe$_{12-2x}$Zn$_x$Zr$_x$O$_{19}$ ($x = 0, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.5, 2.0$) were synthesized via conventional solid-state reaction processes. Precursor powders of SrCO$_3$, Fe$_2$O$_3$, MnCO$_3$, ZnO, ZrO$_2$ (all Kojundo Chemical, Saitama, Japan, 99.9%), and TiO$_2$ (Sigma–Aldrich, 99.9%) were weighed based on the cation ratios of the formulae. The powders were ball-mixed in water, dried, and calcined in air at 1200 °C for 4 h. The calcined samples were ball-milled and calcined again at 1250 °C for 2 h in air to ensure compositional homogeneity. Subsequently, the samples were ground again to fine powders. The hexaferrite powder and epoxy binder (YD014, Kukdo Chemical, Kunshan, Korea) were mixed at a 9:1 wt% ratio, pressed into toroidal-shaped (inner and outer diameters of 3.04 and 7.00 mm, respectively) and disk-shaped (diameter = 15 mm) green compacts, and finally cured at 180 °C for 20 min in air. The volume fraction of the epoxy in the final sample was ~50% [6,7].

X-ray diffraction (XRD, D8 Advance, Bruker AXS GmbH, Germany) with a Cu K$_\alpha$ radiation source ($\lambda = 0.154056$ nm) and field-emission scanning electron microscopy (SEM, JSM-7610F, JEOL, Japan) analyses were performed on second calcined hexaferrite powders for crystalline phase analysis and microstructural observation, respectively. Magnetic properties on the disk-shaped composites were performed by a B–H tracer. The complex permittivity and permeability spectra (100 MHz–18 GHz) of the toroidal-shaped composite samples were measured using a vector network analyzer (E5063A, Keysight, Santa Rosa, CA, USA) with an airline kit (85051BR03) and N1500A software.
3. Results and Discussion

Figure 1a–c shows the XRD patterns of the Zn–Ti, Mn–Ti, and Zn–Zr substituted SrM (0 \( \leq x \leq 2.0 \)) powders after second calcination at 1250 °C. The diffraction peaks of the samples were indexed based on the international center for diffraction data (PDF search number; SrM: 00-033-1340) and the hexagonal magnetoplumbite structure with the space group \( P6_3/mmc \) (ICDD 0801198). As shown in Figure 1a, Zn–Ti substituted SrM (Zn–Ti:SrM) exhibits a single M-type hexaferrite. It is believed that Zn–Ti is fully soluble in the SrM phase in the substitution range of \( x \leq 2.0 \). For the case of Mn–Ti:SrM shown in Figure 1b, a single M-type phase can be identified for \( x \leq 1.5 \) and a small number of second phase peaks of Fe\(_2\)TiO\(_5\) can be observed. Unidentified secondary phase peaks are denoted by an asterisk (*). Unlike Zn–Ti and Mn–Ti:SrM, Zn–Zr:SrM exhibits large second phase peaks of ZnFe\(_2\)O\(_4\), SrZrO\(_3\), and ZrO\(_2\) for \( x \geq 1.5 \) in Figure 1c. For \( x = 2.0 \), ZrFe\(_2\)O\(_4\) exhibits a primary peak. In order to reveal the solubility limit of Zn–Zr (\( x \)) in SrM, additional XRD analysis was carried out on samples with \( x \) between 0.6 and 1.1 with an interval of 0.1. A clear second phase peak of the ZrFe\(_2\)O\(_4\) phase starts appearing at \( x = 1.0 \) and its intensity grows larger with increasing \( x \). In the inset of Figure 1c, the (220) peaks of the samples around \( \theta = 65° \) are presented. Going from \( x = 0 \) to \( x = 0.5 \), the peak shift to the left is large, and the peak position slightly moves to the left between \( x = 0.5 \) and \( x = 1.0 \), but beyond that the peak position does not change. For all samples shown in Figure 1a–c, the lattice parameters, \( a \) and \( c \), are calculated from the values of \( d_{hkl} \) corresponding to the (2011) and (220) peaks according to the following equation:

\[
d_{hkl} = \left\{ \frac{4(h^2 + hk + k^2)}{3a^2} + \frac{l^2}{c^2} \right\}^{-1/2},
\]

where \( d_{hkl} \) is the interplanar spacing, and \( h, k, \) and \( l \) are the Miller indices. The values of \( a, c \), and the cell volume of the sample are listed in Table 1, and their % changes are plotted in Figure 2a–c.

### Table 1. Lattice parameters \( a \) and \( c \), ratio of \( c/a \), and lattice volume of the SrFe\(_{12-2x}\)Zn\(_x\)Ti\(_x\)O\(_{19}\), SrFe\(_{12-2x}\)Mn\(_x\)Ti\(_x\)O\(_{19}\) \( (x = 0, 0.5, 1.0, 1.5, 2.0) \), and SrFe\(_{12-2x}\)Zn\(_x\)Zr\(_x\)O\(_{19}\) \( (x = 0, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.5, 2.0) \) samples calcined at 1250 °C.

| Composition       | \( x \) | \( a(\text{Å}) \) | \( c(\text{Å}) \) | \( \frac{c}{a}(\text{Å}) \) | vol(Å³) |
|-------------------|--------|------------------|------------------|--------------------------|--------|
| SrFe\(_{12-2x}\)Zn\(_x\)Ti\(_x\)O\(_{19}\) | 0      | 5.883            | 23.06            | 3.919                    | 691.0  |
|                   | 0.5    | 5.884            | 23.06            | 3.919                    | 691.2  |
|                   | 1      | 5.890            | 23.06            | 3.916                    | 693.0  |
|                   | 1.5    | 5.892            | 23.07            | 3.916                    | 693.4  |
|                   | 2      | 5.896            | 23.09            | 3.916                    | 695.1  |
| SrFe\(_{12-2x}\)Mn\(_x\)Ti\(_x\)O\(_{19}\) | 0      | 5.882            | 23.04            | 3.916                    | 690.2  |
|                   | 0.5    | 5.892            | 23.07            | 3.915                    | 693.4  |
|                   | 1      | 5.893            | 23.09            | 3.917                    | 694.3  |
|                   | 1.5    | 5.898            | 23.09            | 3.915                    | 695.8  |
|                   | 2      | 5.901            | 23.11            | 3.915                    | 696.8  |
| SrFe\(_{12-2x}\)Zn\(_x\)Zr\(_x\)O\(_{19}\) | 0      | 5.883            | 23.06            | 3.919                    | 691.0  |
|                   | 0.5    | 5.905            | 23.22            | 3.932                    | 701.3  |
|                   | 0.6    | 5.909            | 23.27            | 3.938                    | 703.4  |
|                   | 0.7    | 5.913            | 23.30            | 3.941                    | 705.5  |
|                   | 0.8    | 5.917            | 23.32            | 3.942                    | 707.2  |
|                   | 0.9    | 5.920            | 23.36            | 3.946                    | 709.2  |
|                   | 1      | 5.921            | 23.36            | 3.945                    | 709.4  |
|                   | 1.1    | 5.922            | 23.36            | 3.945                    | 709.6  |
|                   | 1.5    | 5.922            | 23.37            | 3.945                    | 709.7  |
|                   | 2      | 5.922            | 23.35            | 3.943                    | 709.3  |
Figure 1. XRD patterns of (a) SrFe$_{12-2x}$Zn$_x$Ti$_x$O$_{19}$ ($x = 0, 0.5, 1.0, 1.5, 2.0$), (b) SrFe$_{12-2x}$Mn$_x$Ti$_x$O$_{19}$ ($x = 0, 0.5, 1.0, 1.5, 2.0$), and (c) SrFe$_{12-2x}$Zn$_x$Zr$_x$O$_{19}$ ($x = 0, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.5, 2.0$) samples.
Figure 1. Changes (%) in lattice parameters \( a, c \), and cell volume of (a) \( \text{SrFe}_{12-2x}\text{Zn}_x\text{Ti}_2\text{O}_{19} \), (b) \( \text{SrFe}_{12-2x}\text{Mn}_x\text{Ti}_2\text{O}_{19} \) (\( x = 0, 0.5, 1.0, 1.5, 2.0 \)), and (c) \( \text{SrFe}_{12-2x}\text{Zn}_x\text{Zr}_2\text{O}_{19} \) (\( x = 0, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.5, 2.0 \)) samples.

For \( \text{Zn}–\text{Ti} \) and \( \text{Mn}–\text{Ti} \) substitution (\( 0 \leq x \leq 2.0 \)), shown in Figure 2a,b, the lattice volume increases with increasing \( x \). Meanwhile, for the \( \text{Zn}–\text{Zr} \) substitution shown in Figure 2c, the increase in lattice parameters with \( x \) is much greater, but at \( x = 1.0 \) and above, the cell parameter values are constant. Based on the lattice changes with substitution amount \( x \), the solubility limit for \( \text{Zn}–\text{Ti} \) and \( \text{Mn}–\text{Ti} \) is estimated to be above \( x = 2.0 \), and for \( \text{Zn}–\text{Zr} \), it is estimated to be \( x = \sim 1.0 \).

The high-frequency permeability characteristics of the three groups of samples, \( \text{SrFe}_{12-2x}\text{Zn}_x\text{Ti}_2\text{O}_{19} \), \( \text{SrFe}_{12-2x}\text{Mn}_x\text{Ti}_2\text{O}_{19} \), and \( \text{SrFe}_{12-2x}\text{Zn}_x\text{Zr}_2\text{O}_{19} \), were evaluated. In the case of hexaferrites, utilization as an EM absorber in the GHz range requires a peak increase in \( \mu'' \) in the corresponding frequency band, which can be caused by FMR phenomena. Figure 3a–f show the \( \mu' \) and \( \mu'' \) spectra of these samples. As can be seen in the \( \mu' \) spectra, the samples have \( \mu' \) values between 1.5 and 2.0, and \( \mu' \) commonly decreases to close to 1.0 in the range of \( f < 1 \) GHz. This \( \mu' \) spectral transition (\( f < 1 \) GHz) is associated with magnetic domain wall motion [21]. In addition, the transition of \( \mu'' \) in the frequency range of \( f < 1 \) GHz corresponds to the magnetic loss associated with magnetic domain wall motion. Therefore, it is believed that domain wall motion cannot contribute to the permeability at frequencies higher than 1 GHz, and the peak increase of \( \mu' > 1 \) and \( \mu'' > 0 \) at \( f > 1 \) GHz is mostly caused by electron spin motions, that is, FMR [6,7]. It is known that non-substituted M-type Sr-hexaferrite, \( \text{SrFe}_{12}\text{O}_{19} \), has \( f_{\text{FMR}} \sim 50 \) GHz. Thus, no \( \mu'' \) peak is observed in the measured frequency range of \( f \leq 18 \) GHz. When \( \text{Zn}–\text{Ti} \) is substituted into \( \text{SrM} \), \( f_{\text{FMR}} \) decreases with increasing \( x \). In Figure 3a,b, sharp increases in the \( \mu', \mu'' \) peaks can be observed at the right edge. We can see that \( f_{\text{FMR}} \) is approximately 18 GHz for \( \text{SrFe}_{12-2x}\text{Zn}_x\text{Ti}_2\text{O}_{19} \) (\( x = 2.0 \)), and that it is above 18 GHz for samples with \( x < 2.0 \). For the case of \( \text{Mn}–\text{Ti} \) substitution (Figure 3c,d), no clear peaks of \( \mu', \mu'' \) spectra are absorbed at \( f > 1.0 \) GHz for all samples. Meanwhile, a clear FMR signal is absorbed by the \( \text{Zn}–\text{Zr} \) substituted samples, as shown in Figure 3e,f. In the vicinity of 10 GHz in the \( \mu'' \) spectra, a peak from FMR is shown for \( x = 1.0 \), and the height gradually decreases as \( x \) reaches 2.0. For the sample with \( x = 0.5 \), there is no FMR peak at \( f > 1 \) GHz because its \( f_{\text{FMR}} \) is greater than 18 GHz. Although the FMR peak is supposed to shift to a lower frequency upon increasing \( x \) to 1.5, and 2.0, its position is almost the same. This is because even for \( x \) higher than 1.0, no substitution of \( \text{Zn}–\text{Zr} \) can occur, as mentioned previously in Figure 2c. In addition, the decrease in \( \mu'' \) peak height with an increase in \( x \) up to 2.0 is due to an increase in the volume fraction of the non-magnetic secondary phase (Figure 1c).
Figure 3. Real and imaginary part of permittivity ($\mu'$ and $\mu''$) spectra ($0.1 \leq f \leq 18$ GHz) of the hexaferrites, (a,b) SrFe$_{12-2x}$Zn$_x$Ti$_x$O$_{19}$, (c,d) SrFe$_{12-2x}$Mn$_x$Ti$_x$O$_{19}$, (e,f) SrFe$_{12-2x}$Zn$_x$Zr$_x$O$_{19}$ ($x = 0, 0.5, 1.0, 1.5, 2.0$) powder-epoxy (10 wt%) composites.

Figure 4a–e show microstructures of the SrFe$_{12-2x}$Zn$_x$Zr$_x$O$_{19}$ ($x = 0, 0.5, 1.0, 1.5, 2.0$) samples calcined at 1250 °C. The average grain size ($d_g$) roughly decreased with increasing $x$ ($d_g = 1.0, 1.0, 0.82, 0.80, \text{and} 0.65 \mu m$ for $x = 0, 0.5, 1.0, 1.5, \text{and} 2.0$, respectively). It is notable that samples with $x \leq 1.0$ only have a single M-type phase. Second phases (ZnFe$_2$O$_4$, SrZrO$_3$, and ZrO$_2$) are formed and increase with increasing $x$ for $x > 1.0$, as shown in Figure 1c. SEM-BSE (back scattered electron) images of the $x = 1.0, 1.5, \text{and} 2.0$ samples are shown in Figure 4f–h. In the $x = 1.0$ sample (Figure 4f), all grains show nearly equal contrast, but brighter grains begin to appear at $x = 1.5$ (Figure 4g), and brighter spots increase at $x = 2.0$ (Figure 4h). Considering the XRD analysis results (Figure 1c) and average atomic weights of the second phases, the bright spots in Figure 4g,h correspond with SrZrO$_3$.

Figure 5 shows the magnetization curves for the SrFe$_{12-2x}$Zn$_x$Zr$_x$O$_{19}$–epoxy composition ($x = 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1$) samples. Because the solubility limit of
SrFe_{12−2x}Zn_xZr_xO_{19} was found to be approximately x = 1.0, sample compositions with smaller intervals of x below x = 1.0 (x = 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1) were also studied. The saturation magnetization (4πMs) and coercivity (H_C) values of these samples are presented in Table 2. The 4πM–H curves in the low magnetic field range are shown in the inset. The 4πMs of the sintered samples are expected to be twice these values because the volume fraction of the nonmagnetic epoxy binder is ~50%. The 4πMs of the x = 0.5 sample is 1.875 kG, and it decreases with increasing x. The reason for this is that non-magnetic ions of Zn^{2+}, Zr^{4+} are substituted for the magnetic Fe^{3+} ions. It has also been reported that a small amount of Zn substitution (x ≤ 0.3) into SrM could increase Ms due to a selective substitution of Fe in the down-spin state [22,23]. It is notable that the substitution amount (x ≥ 0.5) in this study is too high to expect such an enhancement of Ms in the SrM. H_C decreases noticeably for an increase in x from x = 0.5 to x = 0.7 but decreases slightly from x = 0.7 to x = 0.9 and remains roughly constant above x = 0.9. The H_C value depends on both the intrinsic and extrinsic characteristics of the magnetic materials. Grain size is a dominating factor influencing H_C. It is well known that H_C decreases with increasing grain size of hexaferrites [24–26]. Considering that the average grain size of the x = 0.5 sample is larger than that of the sample with x = 1.0, the smaller H_C for a higher x is due to a strong intrinsic property change caused by the Zn–Zr substitution, which overcomes the disadvantageous extrinsic factor.

![Figure 4](image-url)  
Figure 4. (a–e) SEM micrographs of SrFe_{12−2x}Zn_xZr_xO_{19} (x = 0, 0.5, 1.0, 1.5, 2.0) powder samples calcined at 1250 °C. (f–h) BSE images of SrFe_{12−2x}Zn_xZr_xO_{19} with x = 1.0, 1.5, and 2.0 calcined at 1250 °C.

![Figure 5](image-url)  
Figure 5. M–H curve of SrFe_{12−2x}Zn_xZr_xO_{19}–epoxy composition (x = 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1) samples calcined at 1250 °C (−15 kOe ≤ H ≤ 15 kOe).

The real and imaginary parts of the complex permittivity (ε′ and ε″) and permeability (μ′ and μ″) spectra of the SrFe_{12−2x}Zn_xZr_xO_{19} (x = 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1) powder−
epoxy (10 wt%) composite samples are shown in Figure 6a–d. In Table 2, the real ($\varepsilon'$) and imaginary ($\varepsilon''$) parts of the permittivity at 1 GHz, the real part of the permeability ($\mu'$) in the steady region after the first transition (~3 GHz), and the frequencies of the maximum $\mu''$ values ($f_{\text{FMR}}$) are presented. In the $\varepsilon'$ and $\varepsilon''$ spectra shown in Figure 6a,b, as the frequency increases, for all samples, $\varepsilon'$ decreases and converges upon ~7, and $\varepsilon''$ approaches zero. The real ($\mu'$) and imaginary ($\mu''$) parts of the permeability spectra are shown in Figure 6c,d, the first transitions of $\mu'$ and $\mu''$ are associated with magnetic domain wall motion ($f < 2$ GHz), and the peaks at higher frequencies ($f > 2$ GHz) are caused by FMR. In the $\mu''$ spectra (Figure 6d), a gradual $\mu''$ peak shift to the left is observed upon increasing $x$ from 0.7 to 0.9, and a very small peak shift can be found between $x = 0.9$ and $x = 1.0$. The $\mu''$ peak frequency corresponds to $f_{\text{FMR}}$ and is directly proportional to the magnetic anisotropy field ($H_a$), as expressed in Equation (1). The change in $f_{\text{FMR}}$ is related to an intrinsic property change and can be caused by cation substitution. This is consistent with the change in $H_C$ shown in Figure 5, as mentioned above. The $\mu''$ peak positions and $H_C$ values of the samples with $x = 0.9–1.1$ are very similar, because the solubility limit of Zn–Zr in the M-phase is approximately $x = 1.0$. The gradual increase in $\mu'$ upon increasing $x$ up to 0.9 can be explained by Snoek's limit law [27], presented below:

$$ (\mu' - 1) f_{\text{FMR}} = \frac{2}{3} \gamma - 4 \pi M_S \sinh^{-1}(x) $$ (3)

**Table 2.** Saturation magnetization ($4\pi M_S$), coercivity ($H_C$), real ($\varepsilon'$) and imaginary ($\varepsilon''$) parts of permittivities at 1 GHz, real part of permeability ($\mu'$) at steady region (at 3 GHz), frequencies of maximum $\mu''$ values ($f_{\text{FMR}}$), minimum RLs ($RL_{\text{min}}$), and frequencies of $RL_{\text{min}}$ ($f_{RL_{\text{min}}}$) of SrFe$_{12-2x}$Zn$_x$Zr$_x$O$_{19}$ ($x = 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1$) powder–epoxy (10 wt%) composite samples.

| $x$ | $4\pi M_S$ (kG) | $H_C$ (kOe) | $\varepsilon'$ (1 GHz) | $\varepsilon''$ (1 GHz) | $\mu'$ (3 GHz) | $f_{\text{FMR}}$ (GHz) | $RL_{\text{min}}$ (dB) | $f_{RL_{\text{min}}}$ (GHz) |
|-----|----------------|-------------|----------------------|-----------------------|---------------|----------------------|----------------------|----------------------|
| 0.5 | 1.875          | 0.624       | 7.37                 | 1.08                  | 1.00          | -                    | -                    | -                    |
| 0.6 | 1.810          | 0.466       | 7.32                 | 0.82                  | 1.02          | -                    | -                    | -                    |
| 0.7 | 1.681          | 0.270       | 7.08                 | 0.45                  | 1.05          | 15.1                 | -42.9                | 16.7                 |
| 0.8 | 1.607          | 0.225       | 7.34                 | 0.51                  | 1.12          | 10.8                 | -38.6                | 11.8                 |
| 0.9 | 1.409          | 0.158       | 7.16                 | 0.21                  | 1.19          | 8.33                 | -44.7                | 8.8                  |
| 1.0 | 1.295          | 0.135       | 6.85                 | 0.20                  | 1.17          | 7.89                 | -49.7                | 8.6                  |
| 1.1 | 1.191          | 0.152       | 7.02                 | 0.13                  | 1.17          | 7.26                 | -50.0                | 8.2                  |

![Figure 6. (a-d) Real and imaginary parts of permittivity ($\varepsilon'$ and $\varepsilon''$) and permeability ($\mu'$ and $\mu''$) spectra (100 MHz $\leq f \leq$ 18 GHz) of SrFe$_{12-2x}$Zn$_x$Zr$_x$O$_{19}$ ($x = 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1$) powder–epoxy (10 wt%) composite samples.](image-url)
Here, $\gamma$ is a constant known as the gyromagnetic ratio, and $M_s$ is the saturation magnetization value. A decrease in static real permeability ($\mu'$) causes an increase in $f_{FRM}$. This implies that changes in the high-frequency permeability property are governed by the intrinsic magnetic parameter of the magnetocrystalline anisotropy, which can be controlled by Zn–Zr substitution.

According to transmission line theory [28], the reflection loss (RL), which implies the EM wave absorption performance, can be calculated using the following equations:

$$RL (dB) = 20 \log \left( \frac{Z_{in}}{Z_0} - 1 \right) \left( \frac{Z_{in}}{Z_0} + 1 \right)$$  \hspace{1cm} (4)$$

$$Z_{in} = \sqrt{\frac{\mu_r}{\varepsilon_r}} tanh \left[ j \left( \frac{2\pi d}{c} \right) \sqrt{\frac{\mu_r}{\varepsilon_r}} \right]$$  \hspace{1cm} (5)$$

where $Z_{in}$ is the input impedance of the absorber, $Z_0 = \sqrt{\mu_0\varepsilon_0}$ is the characteristic impedance of free space, $c$ is the speed of light, $f$ is the frequency of the incident EM wave, $d$ is the thickness of the absorber, and $\varepsilon_r$ and $\mu_r$ are the complex permittivity ($\varepsilon_r = \varepsilon' - j\varepsilon''$) and permeability ($\mu_r = \mu' - j\mu''$), respectively. Here, the measured $\mu'$, $\mu''$, $\varepsilon'$, and $\varepsilon''$ spectra can be used to obtain $\frac{Z_{in}}{Z_0}$ for any thickness $d$ with respect to $f$. RL calculations were plotted in square $f$–$d$ maps, as shown in Figure 7a–d. The region in which $RL \leq -10$ dB, which implies EM absorptions exceeding 90%, is outlined by solid black lines. Inside this area, the regions in which $RL \leq -20$, −30, and −40 dB are also outlined by solid lines.

![Image](image-url)

**Figure 7.** (a–i) RL map as functions of sample thickness ($d$) and frequency ($f$) for SrFe$_{12-2x}$Zn$_x$Zr$_x$O$_{19}$ ($x = 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.5, 2.0$) powder–epoxy (10 wt%) composite samples.

In the RL map shown in Figure 7a–i, the strong EM absorbing area at lower $d$, marked with a rectangular box, starts to be observed at $x = 0.7$, and it moves gradually with an
increase in $x$ up to 1.0 (Figure 7c–f). The left edge of the absorption area already appeared at the right edge of Figure 7b for the sample with $x = 0.6$. EM absorption in the marked area is caused by a magnetic loss mechanism, that is, FMR, which produces a peak in the $\mu''$ spectra. Thus, the gradual movement of the EM absorbing area with $x = 0.7, 0.8,$ and 0.9 (Figure 6c–e) is attributed to the $\mu''$ peak shift shown in Figure 6d. It is also observed that the absorption intensity in the RL maps for $x$ from 1.1 to 2.0 (Figure 6g–i) becomes weaker. A decrease in the $\mu''$ peak height shown in Figure 3f is the reason for the weakening EM absorption. As previously mentioned, the decrease in $\mu''$ peak height for the $x = 1.5$ and 2.0 samples is due to an increase in the non-magnetic second phase.

Figure 8 shows the RL spectra of the sample ($x = 0.7, 0.8, 0.9, 1.0, 1.1$) at the optimal thickness, at which the minimum RL ($RL_{\text{min}}$) point was located. The $RL_{\text{min}}$ values and frequency of $RL_{\text{min}}$ ($f_{RL_{\text{min}}}$) are presented in Table 2. Each sample shows an $RL_{\text{min}} < -30$ dB, and $f_{RL_{\text{min}}}$ shifts to a lower frequency with increasing $x$. $f_{RL_{\text{min}}}$ shifts to a lower $f$ in large steps as $x$ increases from 0.7 to 0.9, but it moves only slightly at $x \geq 0.9$. The tendency for changes in large steps up to $x = 0.9$, and then for changes in very small steps for $x > 0.9$, is the same for $H_C$, $f_{FMR}$, and $RL_{\text{min}}$. All these changes are related to the Zn–Zr substitution amount in the M-type phase and its magnetocrystalline anisotropy change. As shown, $f_{RL_{\text{min}}}$ is similar to $f_{FMR}$ for each sample, and FMR is the dominant EM absorbing mechanism in hexaferrites. The $x = 0.9$ sample demonstrates EM absorption properties optimized for the X-band (8–12 GHz) with the lowest reflection loss (RL) of $-45$ dB and satisfying $RL < -15$ dB in the 8–13 GHz range, whereas the sample with $x = 0.8$ shows an excellent Ku band (12–18 GHz) absorption performance, satisfying $RL < -19$ dB in the 11–18 GHz range.

![Figure 8. RL vs. f plot of SrFe$_{12-2x}$Zn$_x$Zr$_x$O$_{19}$ ($x = 0.7, 0.8, 0.9, 1.0, 1.1$) powder–epoxy composites for determining optimal absorber thickness (mm).](image-url)

### 4. Conclusions

From among the three different $M_1^{2+}$–$M_2^{4+}$ substitutions of Mn–Ti, Zn–Ti, Zn–Zr, the Zn–Zr substitution most effectively decreased the intrinsic property of the magnetocrystalline anisotropy of the hexaferrite, although the solubility limit ($x = \sim 1.0$) is smaller than that for the other substitutions. The coercivity, natural resonance frequency, and frequency range of the EM absorption via the magnetic loss mechanism decreased in large steps for an increasing substitution $x$ of up to 0.9, and then decreased slightly with increasing $x$ for $1.0 \leq x \leq 1.1$. All these parameters are closely related to one another, and the changes are due to the magnetic crystalline anisotropy caused by the Zn–Zr substitution. The sample with $x = 0.9$ demonstrated a high EM absorption in the X-band (8–12 GHz) with the lowest reflection loss of $<-45$ dB, and the sample with $x = 0.8$ exhibited a broad Ku band (12–18 GHz) absorption performance satisfying $RL < -19$ dB at $11 \leq f \leq 18$ GHz. Herein, we report for the first time the EM absorption properties of Zn–Zr substituted M-type Sr-hexaferrites and show that they are very promising candidates for X and Ku band EM absorbers.
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