

Nickel and Copper Doping in M-Type Strontium Hexaferrite ($\text{SrFe}_{12}\text{O}_{19}$): A Review of Structural, Magnetic and Dielectric Properties

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Abstract

Strontium hexaferrite ($\text{SrFe}_{12}\text{O}_{19}$), commonly designated as SrM, is an important M-type hexagonal ferrite because of its high coercivity, strong uniaxial magneto crystalline anisotropy, chemical stability, good thermal stability and relatively low production cost. These characteristics have resulted in widespread interest in SrM for permanent magnets, magnetic recording, sensors, electromagnetic interference shielding and microwave devices. Nevertheless, further improvement and functional diversification of $\text{SrFe}_{12}\text{O}_{19}$ require controlled modification of its crystal structure, magnetic exchange interactions and microstructure. Cation substitution is one of the most effective approaches for achieving such modification. In particular, Ni^{2+} and Cu^{2+} substitution at Fe^{3+} sites can alter lattice parameters, crystallographic site occupancy, magnetic anisotropy, saturation magnetization, coercivity, dielectric relaxation and microwave response. The literature indicates that Ni substitution generally produces lattice contraction and can decrease saturation magnetization because of changes in Fe–O–Fe exchange interactions. However, the effect on coercivity depends strongly on dopant concentration, particle size and microstructure. Cu substitution exhibits more complex concentration-dependent behaviour, with optimized compositions showing substantial enhancement in coercivity and changes in saturation magnetization. Cu incorporation can also influence oxygen-vacancy concentration, dielectric loss and microwave absorption. The available evidence demonstrates that synthesis route, crystallite size, lattice strain, cation distribution and secondary-phase formation must be considered together when interpreting dopant effects. Although considerable research has been conducted on individual Ni- and Cu-substituted SrM, direct systematic investigation of Ni–Cu co-doped $\text{SrFe}_{12}\text{O}_{19}$ remains limited. The composition $\text{SrFe}_{12-x-y}\text{Ni}_x\text{Cu}_y\text{O}_{19}$ therefore provides a promising research platform for developing multifunctional rare-earth-free magnetic materials.

Keywords: $\text{SrFe}_{12}\text{O}_{19}$; strontium hexaferrite; M-type hexaferrite; Ni^{2+} substitution; Cu^{2+} substitution; cation distribution; magnetic properties; dielectric properties.

1. Introduction

Hexagonal ferrites are important ferrimagnetic ceramics because their magnetic, electrical and dielectric properties can be tailored through composition and processing. Among them, M-type strontium hexaferrite ($\text{SrFe}_{12}\text{O}_{19}$) is widely studied due to its high coercivity, strong uniaxial anisotropy, chemical stability, corrosion resistance and low cost [1–4]. It is also attractive for sustainable permanent-magnet applications because it does not require rare-earth elements [1,2]. $\text{SrFe}_{12}\text{O}_{19}$ has a hexagonal magneto plumbite structure with space group $P6_3/mmc$, in which Fe^{3+} ions occupy five inequivalent sites: 2a, 2b, 12k, 4f₁ and 4f₂ [3–5]. Its magnetic properties depend strongly on crystallite size, morphology, strain, grain boundaries and synthesis conditions [2,6–8]. Various methods, including solid-state, sol-gel, combustion and hydrothermal techniques, have been employed to control these parameters [6–10]. Transition-metal substitution, particularly with Ni^{2+} and Cu^{2+} , provides an effective route for modifying structural, magnetic, dielectric and microwave properties [11–18]. This review focuses on the effects of Ni and Cu substitution and identifies research opportunities in Ni–Cu co-doped $\text{SrFe}_{12}\text{O}_{19}$.

2. Crystal Structure and Magnetic Characteristics of $\text{SrFe}_{12}\text{O}_{19}$

M-type $\text{SrFe}_{12}\text{O}_{19}$ has a hexagonal magneto plumbite structure consisting of alternating spinel-like (S) and hexagonal (R) blocks along the c-axis [4,5]. Sr^{2+} occupies the large cationic site, while Fe^{3+} ions are distributed among five non-

equivalent sites (2a, 2b, 12k, 4f₁ and 4f₂). The different spin orientations of these Fe sites produce the characteristic ferrimagnetic behaviour of SrM [4,5]. Consequently, substitution of Fe³⁺ by other metal ions can alter the net magnetic moment depending on their preferred crystallographic positions. The magnetic properties are also influenced by particle size, morphology, strain and grain boundaries [7,8]. Plate-like or hexagonal particles can provide favourable magnetic anisotropy and improve magnetic performance. In addition, crystallite size affects domain-wall movement and coercivity, with excessive grain growth generally promoting multidomain behaviour [7,8]. Therefore, synthesis conditions strongly influence phase formation, particle morphology and the resulting magnetic properties [6,8–10].

3. Comparison of Ni and Cu Substitution

Ni²⁺ and Cu²⁺ are both divalent transition-metal ions, but their influence on SrFe₁₂O₁₉ is not identical. Their different electronic structures, magnetic moments and crystallographic site preferences lead to different structural and magnetic responses.

Ni substitution is strongly associated with lattice contraction and reduction in saturation magnetization at increasing concentrations [13,14]. Direct neutron-diffraction evidence indicates preferential occupation of the 12k site, providing a structural explanation for changes in magnetic exchange [14].

Cu substitution produces a more complex response. Its influence on coercivity can be particularly strong at selected concentrations, while saturation magnetization may exhibit non-monotonic behaviour [17]. Cu can additionally influence oxygen-vacancy concentration and dielectric loss [16–19].

Research published shows that Ni and Cu substitution can effectively tailor the structural and functional properties of M-type SrFe₁₂O₁₉. Ni²⁺ substitution generally causes lattice contraction and may reduce saturation magnetization by altering Fe–O–Fe exchange interactions. Recent neutron-diffraction results indicate preferential Ni occupation at the 12k site, while increasing Ni content can influence saturation magnetization, coercivity and thermal behaviour [12–14]. Ni substitution also affects the electrical and dielectric response of SrM. Cu²⁺ substitution produces more concentration-dependent changes in magnetic behaviour. It can modify lattice strain, oxygen-vacancy concentration, phase formation and magnetic exchange interactions [16–19]. Optimized Cu concentrations have been associated with enhanced coercivity and altered saturation magnetization [17]. Cu-containing substituted SrM has also shown promising microwave absorption characteristics [20].

4. Dielectric and Electrical Properties

Although SrFe₁₂O₁₉ is principally studied as a hard magnetic material, its electrical and dielectric characteristics are increasingly important for high-frequency and multifunctional applications.

The dielectric response of ferrites is generally associated with charge polarization, electron hopping and interfacial effects. In iron-containing ferrites, electron hopping between Fe²⁺ and Fe³⁺ can contribute to AC conductivity, while grain boundaries can dominate the low-frequency dielectric response [13,19].

Ni substitution has been shown to modify dielectric constant, dielectric loss and electrical resistivity [12,13]. These changes can result from altered defect concentration, local charge compensation and changes in the Fe²⁺/Fe³⁺ hopping mechanism.

The Ni-doped system investigated through microemulsion synthesis exhibited frequency-dependent dielectric behaviour and increased dielectric parameters with substitution at lower frequencies [12]. Such behaviour suggests that Ni incorporation affects both polarization and electrical conduction.

Cu substitution also influences dielectric behaviour. Cu-induced changes in oxygen-vacancy concentration and electronic structure can contribute to dielectric relaxation and frequency-dependent conductivity [16,19]. Recent Cu–Gd co-substituted SrM has demonstrated modified magneto-dielectric behaviour, indicating that Cu-containing compositions may be suitable for multifunctional electronic devices [19].

The simultaneous control of magnetic and dielectric losses is particularly relevant for microwave applications. A material with suitable permeability and permittivity can provide impedance matching and electromagnetic attenuation.

5. Research Gap: Ni–Cu Co-Doping

The literature clearly demonstrates that both Ni and Cu can modify $\text{SrFe}_{12}\text{O}_{19}$. However, direct systematic investigation of simultaneous Ni–Cu substitution remains comparatively limited.

Several related co-substitution systems have already been investigated. La–Cu and La–Ni co-substitution provides an especially relevant example because divalent Cu^{2+} or Ni^{2+} is introduced simultaneously with trivalent La^{3+} [21]. This approach demonstrates that coupled substitution can be used to control both charge balance and magnetic properties.

The La–Cu/La–Ni comparative study is particularly significant because it investigated both Cu and Ni under similar experimental conditions. The results demonstrated that the two dopants do not produce identical magnetic responses, confirming the importance of dopant-specific electronic and structural effects [21]. However, a direct Ni–Cu co-doped system of the general composition $\text{SrFe}_{12-x-y}\text{Ni}_x\text{Cu}_y\text{O}_{19}$. The effect of Ni–Cu co-substitution therefore cannot be predicted simply by adding the individual effects of Ni and Cu. A systematic composition matrix should be used to determine whether the two dopants produce additive, synergistic or antagonistic behaviour.

6. Future Research Directions

Future work should focus on developing a complete structure–microstructure–property relationship for Ni–Cu substituted $\text{SrFe}_{12}\text{O}_{19}$. The first priority should be determination of the crystallographic distribution of Ni and Cu. Recent neutron-diffraction evidence for Ni occupation of the 12k site demonstrates the importance of site-specific analysis [14].

The second priority should be investigation of defect chemistry. Because Ni^{2+} and Cu^{2+} substitute for Fe^{3+} , charge compensation may occur through oxygen vacancies or changes in iron valence. Such defects can simultaneously influence magnetic exchange and electrical conductivity.

The third priority should be optimization of crystallite size. The best magnetic properties are not necessarily obtained from the smallest particles. Particle size must be controlled within a range that supports strong magnetic ordering and suitable domain structure.

The fourth priority should be multifunctional characterization. The same composition should be evaluated for structural, magnetic, dielectric properties so that the relationships among these characteristics can be established.

7. Conclusion

The substitution of transition-metal and rare-earth ions is an effective approach for tailoring the structural, magnetic, dielectric and microwave-absorption properties of M-type strontium hexaferrite ($\text{SrFe}_{12}\text{O}_{19}$). Ni^{2+} substitution generally modifies the lattice parameters, crystallographic site occupancy, magnetic exchange interactions and electrical response, while Cu^{2+} substitution produces concentration-dependent changes in lattice strain, oxygen vacancies, phase formation and magnetic behaviour. Suitable Ni and Cu concentrations can improve selected properties, such as coercivity, dielectric response and microwave absorption. However, excessive substitution may lead to secondary phases and undesirable changes in magnetic performance. Therefore, careful control of dopant concentration, synthesis conditions and cation distribution is essential for obtaining the required properties. These findings demonstrate the potential of Ni- and Cu-substituted strontium hexaferrite for applications in permanent magnets, electromagnetic-interference shielding and microwave-absorbing materials.

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