Materials Research Express

PAPER

Electromagnetic wave absorption performance of Ni doped Cu-ferrite nanocrystals

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Keywords: Ni1xCu1−xFe2O4, spinel structure, magnetic properties, dielectric properties, electromagnetic wave absorption properties

Abstract

Ni1xCu1−xFe2O4 nanocrystals were prepared by co-precipitation technique to study the electromagnetic (EM) wave absorption properties. The XRD and SEM results confirm the formation of single-phase cubic spinel structure and reveal that the crystallite size decreases with the addition of Ni content. The vibrating sample magnetometer results showed that the as-prepared material was soft magnetic and have potential applications in magnetic storage technology and field sensors. The dielectric parameters and EM wave absorption characteristics of Ni1xCu1−xFe2O4 nanocrystals were studied in the frequency range of 1-18GHz using a vector network analyzer. The permittivity, impedance matching, and EM wave absorption of the materials are significantly improved with the increase in Ni content. The lowest value of reflection loss (RL) is observed −22.8 dB at 16.09 GHz (RL ≤ −10dB, absorption >90%), showing an optimal EM wave absorption performance, which might generate from the synergistic effect between relative permittivity and permeability.

1. Introduction

Recently, with the rapid development of information technology and communication devices, the EM radiation and interferences have become a huge problem for human life and in different electronic device operations [1–7]. The use of different advanced sensors and precision-guided weapons endangers survival and interferes with aerospace weapons related to the stealth technology [8–10]. The elimination of EM interference between EM wave radiating systems and electronic equipment plays a significant impact on practical applications [11–13]. Therefore, the EM wave absorbing materials gain much attention, which can effectively absorb EM wave and convert into thermal or interference-dispersed microwave (MW) [14–16]. Though, it is still a great challenge to develop a novel EM wave absorbers which simultaneously satisfy all the necessities such as broad and strong absorption bandwidth in a wide frequency range, small thickness and light-weight [17–19]. In recent years, nanomaterials have achieved much attention as a unique EM wave absorption materials owing to their high surface energy and small size [20]. Moreover, nano-ferrites offered exceptional properties to be an excellent absorber due to their high absorption efficiency, thin coating, broad frequency bandwidth and low cost [21].

Nickel ferrites (NiFe2O4) as a well-known form of magnetic ferrites shows the unique characteristics of well chemical stability, modest saturation magnetization, and low cost, therefore it has potential applications in the field of EM wave absorption [22–24]. Wei et al synthesized hierarchical carbon@cobalt acid nickel@ferriferrous oxide composites by a simple one-step hydrothermal and co-deposition route [25]. The hybrid and unique void space leads to the efficient dielectric and magnetic loss resulting to increase EM wave absorption properties of the material, with a thickness of 3.4 mm and the lowest value of RL was achieved −43.0 dB at 13.4 GHz. Lv et al
successfully prepared hollow carbon@iron@ferriferrous oxide nanospheres using facile template followed by pyrolysis process [26]. In their research, an optimum $R_c$ of $-40$ dB was detected at a thickness of 1.5 mm at 5.2 GHz. Henceforth, Cu-ferrites with Ni dopant are a significant class of spinel ferrites because of their interesting electromagnetic properties, additionally containing the structural phase transition, attended by a reduction in the crystal symmetry to tetragonal [27]. According to the crystalline structure, Ni-ferrite is an inverse spinel ferrite, which retains high electrical resistivity and low eddy current losses. The replacement of Cu in Ni-ferrite improves its structural properties which are suitable in many applications. Both Ni and Cu ferrites can also play an important role among all magnetic materials due to their high electrical resistivity, saturation magnetization, and magnetic permeability. Previously, the effect of different calcination temperatures has been observed on the structural properties of Ni and Cu nano-crystalline ferrite, prepared through the sol-gel method [28]. Different techniques have been used to synthesize nano-crystalline ferrites such as sol-gel, sonochemical, MW processing, hydrothermal, and co-precipitation techniques, etc by different researchers. Among all these techniques, the co-precipitation technique attracts much more attention to synthesize nano-crystalline ferrite [29]. This technique is a facile and convenient to obtain a uniform composition in two or more cations homogeneous solution through precipitation reaction, which is one of important methods for the synthesis of material containing two or more kinds of metal elements. In this article the nanocrystals with the chemical composition of $\text{Ni}_x\text{Cu}_{1-x}\text{Fe}_2\text{O}_4$ are synthesized by co-precipitation technique and the effects of Ni doping on the EM wave absorption properties are observed. It has been observed that the introduction of the Ni dopants can significantly improve the EM wave absorption performance of the samples. Benefiting from the excellent properties of Ni doped Cu-ferrite nanocrystals are proposed as the high efficient lightweight EM wave absorbers.

2. Experimental procedure

All the reagents used in the experiment were supplied by Sino-pharm Chemical Reagents Co., Ltd, China. Sodium hydroxide (NaOH), di-hydrated copper chloride ($\text{CuCl}_2\cdot2\text{H}_2\text{O}$), high purity hexa-hydrated nickel chloride ($\text{NiCl}_2\cdot6\text{H}_2\text{O}$) and hexa-hydrated ferric chloride were used as raw materials. In order to achieve the desired compositions, stoichiometric aggregates of $\text{CuCl}_2\cdot2\text{H}_2\text{O}$, $\text{NiCl}_2\cdot6\text{H}_2\text{O}$ and $\text{FeCl}_3\cdot6\text{H}_2\text{O}$ were dissolved in distilled water by using magnetic stirrer by an average speed of 900rpm. The precipitant agent sodium hydroxides (NaOH, 2M) were added drop-wise until the pH reached close to 13. During this process, the yellowish green solution converts into dark brown precipitate. The reaction can be expressed as follows:

$$x\text{NiCl}_\cdot6\text{H}_2\text{O} + (1-x)\text{CuCl}_\cdot2\text{H}_2\text{O} + 2\text{FeCl}_3\cdot6\text{H}_2\text{O} + \text{NaOH} \rightarrow \text{Ni}_x\text{Cu}_{1-x}\text{Fe}_2\text{O}_4 + \text{NaCl} + \text{H}_2\text{O}$$

The beakers containing dark brown precipitates were aged into a pre-heated water bath at 90 °C for 2h. The resulted precipitates were centrifuged, washed thoroughly with distilled water and dried at 60 °C overnight in a vacuum oven. The as-prepared precipitate was ground and calcined at 900 °C for 4 h in air.

The phase compositions of as-prepared $\text{Ni}_x\text{Cu}_{1-x}\text{Fe}_2\text{O}_4$ nanocrystals were investigated by XRD (D/MAX-Ultima IV). The morphology of the nanocrystals was analyzed by scanning electron microscopy (SEM, JSM-6380LA). The FT-IR absorption spectra were observed at room temperature by FT-IR spectrometer (Nicolet i550, Thermo Fisher Scientific) in the range of 300–2000 cm$^{-1}$. Magnetic properties were investigated at room temperature with a vibrating sample magnetometer (VSM, JDAW-2000D, Yingpu, China) with a maximum magnetic field 10 kOe. The EM parameters were measured using a vector network analyzer (5244A, Agilent-N, USA) in the frequency range 1–18 GHz.

3. Results and discussion

3.1. Crystal structure and morphology

XRD patterns of $\text{Ni}_x\text{Cu}_{1-x}\text{Fe}_2\text{O}_4$ at compositions of $x = 0, 0.1, 0.3, 0.5, 0.7$ are shown in the figure 1(a). It can be seen that the peaks at $2\theta$ of 18.34°, 30.23°, 35.62°, 37.09°, 43.30°, 53.79°, 57.31°, 62.96° related to the diffraction planes (111), (220), (311), (222), (400), (422), (511) and (440) for all samples [30]. These peaks confirmed that single phase cubic spinel ferrite ($\text{Ni}_x\text{Cu}_{1-x}\text{Fe}_2\text{O}_4$, JCPDS # 77-0010 and 74-2081). Furthermore, a few extra peaks appeared at 34.99° and 38.75° correspond to the Cu(FeO$_2$) and CuO (JCPDS # 79–1546 and 72–0629) respectively. The strong and sharp peaks of diffraction in the XRD patterns indicate high crystallinity in all the samples. The Debye–Scherrer’s equation (equation (1)) was applied to determine the crystallite size from the most intense diffraction peaks (311) [31];
where ‘0.9’ is the Scherrer’s constant depends on how width is determined and it also shows the size distribution and shape of crystal, ‘λ’ is the wavelength of x-ray radiations (\(\lambda = 1.5408 \text{ Å}\)), ‘β’ is the full-width half-maximum of peaks, ‘θ’ is the Bragg angle and ‘D’ is the crystallite size, It can be noted clearly from table 1 that with the increase in Ni content crystallite size decreases, which may ascribe to the lower atomic radius of Ni\(^{2+}\) (0.69 Å) than that of Cu\(^{2+}\) (0.73 Å) [32]. The minimum crystallite size is calculated as 28.55 nm at \(x = 0.5\) (Ni\(_{0.5}\)Cu\(_{0.5}\)Fe\(_2\)O\(_4\)). Following equation (2) was used to calculate the lattice constants for all samples [33];

\[
a = d_{hkl}(h^2 + k^2 + l^2)^{1/2}
\]

Miller indices of the crystal planes are denoted as ‘h, k and l’, whereas ‘\(d_{hkl}\)’ is interplaner spacing. The calculated lattice parameters are shown in table 1. Spinel ferrite is capable of accommodating cations to occupy tetrahedral A-site and octahedral B-site. According to Neel’s sub-lattice model, Cu\(^{2+}\) ions are existing A-site and B-site and Ni\(^{2+}\) occupy B-site, whereas Fe\(^{3+}\) ions transform to Fe\(^{2+}\) ions to attain the charge neutrality. The x-ray density was calculated by using equation (3) [34];

\[
d_x = \frac{8M}{N_a V}
\]

where ‘8’ stands for the number of formula units in a cell, molecular weight is denoted by ‘M’, ‘\(N_a\)’ is Avogadro’s No. and volume of the unit cubic cell is denoted by ‘\(a^3\)’ [34]. The values of x-ray density for Ni\(_x\)Cu\(_{1-x}\)Fe\(_2\)O\(_4\) at \(x = 0, 0.1, 0.3, 0.5, 0.7\) in the table are in close agreement with the literature [35]. The decrease in x-ray density with the increase of Ni content may be due to the higher atomic weight and density of Cu (63.546 g mol\(^{-1}\), 8.96 g cm\(^{-3}\)) than that of Ni (58.933 g mol\(^{-1}\), 8.91 g cm\(^{-3}\)). Following equations (4) and (5) were used to determine the distance between the magnetic ions on A and B sites [30];

\[
d_A = 0.25a\sqrt{3}
\]

\[
d_B = 0.25a\sqrt{2}
\]

where the lattice parameter is denoted by ‘a’. Table 1 constitutes the hopping lengths, tetrahedral \(d_A\) and octahedral \(d_B\) sites. The results are explained on the basis of the variation of the lattice constant with the dopant element [36].

| Samples          | Crystallite size (nm) | Lattice constant (Å) | x-ray density (g/cm\(^3\)) | \(d_A\) (nm) | \(d_B\) (nm) |
|------------------|-----------------------|----------------------|-----------------------------|--------------|--------------|
| Ni\(_x\)Cu\(_{0.5}\)Fe\(_2\)O\(_4\) | 46.68                  | 8.353                | 5.455                        | 0.295        | 0.362        |
| Ni\(_{0.1}\)Cu\(_{0.9}\)Fe\(_2\)O\(_4\) | 41.59                  | 8.338                | 5.473                        | 0.295        | 0.361        |
| Ni\(_{0.3}\)Cu\(_{0.7}\)Fe\(_2\)O\(_4\) | 30.5                   | 8.367                | 5.394                        | 0.296        | 0.362        |
| Ni\(_{0.5}\)Cu\(_{0.5}\)Fe\(_2\)O\(_4\) | 28.55                  | 8.343                | 5.419                        | 0.295        | 0.361        |
| Ni\(_{0.7}\)Cu\(_{0.3}\)Fe\(_2\)O\(_4\) | 37.59                  | 8.349                | 5.385                        | 0.295        | 0.362        |
Figure 1(b) shows the FT-IR spectra for the nanocrystals in the frequency range 300–2000cm. Two principle bands of spinel ferrites $\nu_2$ and $\nu_1$ are observed in the spectra. The $\nu_2$ and $\nu_1$ bands located in the range of 400–410cm$^{-1}$ and 580–600cm$^{-1}$ respectively, which may be due to the pulsation of ions in crystals [37]. The bands $\nu_2$ and $\nu_1$ are assigned to the stretching vibration of octahedral B-sites and tetrahedral A-sites metal oxygen ions, which are bond bending vibrations confirming the presence of single-phase cubic spinel structure and ferrites formation [38]. The $\nu_1$ relates to the stretching vibration of Fe$^{3+}$–O$^{2-}$ in A-site, and $\nu_2$ relates to the stretching vibration of Fe$^{3+}$–O$^{2-}$ in B-site. This variation in the band positions is due to the difference in the Fe$^{3+}$–O$^{2-}$ distances for the tetrahedral and octahedral complexes [39].

Figure 2 shows the SEM images of Ni$_x$Cu$_{1-x}$Fe$_2$O$_4$ nanocrystals at $x = 0$ (a), $x = 0.1$ (b), $x = 0.3$ (c), $x = 0.5$ (d) and $x = 0.7$ (f).

Figure 3 shows the magnetic hysteresis loops (a) and Maximum magnetization values (b) of Ni$_x$Cu$_{1-x}$Fe$_2$O$_4$ nanocrystals at different values of $x$.

3.2. Magnetic properties

Figure 3 shows the magnetic hysteresis loops of Ni$_x$Cu$_{1-x}$Fe$_2$O$_4$ nanocrystals. It can be noted that the increase in the concentration of Ni$^{2+}$ gives rise to an increase in $M_s$ and decrease in $H_c$, which is related to cation distribution in ferrites. In ferromagnetic ferrites magnetic order occurs due to the super-exchange interaction of ions in A- and B-sites. The strong exchange interaction between A and B sites may be the fact of the increase in
saturation magnetization [29]. The decrease in \( H_c \) may be due to the decrease in grain size as shown in the XRD analysis. \( H_c \) is the direct proportion to the volume of single-domain grains. Therefore, \( H_c \) decreases as the single domain particle size decreases [43]. Moreover, the ratio between \( M_s \) and \( M_r \) (\( M_s / M_r \)) also decreased with an increase in Ni content. The low value of \( M_s / M_r \) indicates an appreciable fraction of supermagnetic particles and the presence of spin canting [44].

Therefore, the small grain size ascribes to the higher fraction of surface cation and lower the total hyperfine field, which causes the final decrease in the \( M_s \) [45]. However, the phase transformation from tetragonal to the cubic structure referred to a large increase in saturation magnetization. In this case, some Cu\(^{2+}\) ions occupy A-site, which reduces the tetragonal distortion and the transformations of Fe\(^{3+}\) ions into Fe\(^{2+}\) take place [46]. Hence, the magnetization of A-site decreases, which is similar to the XRD results. This induces a severe change in its magnetic reaction by doubling the effective magnetic moment per unit formula and reduces its crystalline anisotropy [47]. The magnetic moment per formula unit in Bohr magneton (\( \mu_B \)) of Ni\(_x\)Cu\(_{1-x}\)Fe\(_2\)O\(_4\) was calculated by using the following equation (6) [29]:

\[
\eta_B = \frac{M \times M_s}{5585}
\]

(6)

where molecular weight is denoted by ‘M’ and saturation magnetization by ‘\( M_s \)’, equation (7) is used to determine the Magnetic anisotropy (K) [29].

\[
H_c = \frac{0.96K}{M_s}
\]

(7)

where ‘\( H_c \)’ is coercivity and ‘\( M_s \)’ is magnetic saturation. The detailed value of magnetic parameters such as \( M_s \), \( H_c \), \( M_r \), \( M_s / M_r \), \( \eta_B \) and K of Ni\(_x\)Cu\(_{1-x}\)Fe\(_2\)O\(_4\) is illustrated in table 2.

Table 2. The values of magnetic parameters, \( M_s \), \( H_c \), \( M_r \), \( M_s / M_r \), \( \eta_B \) and K of Ni\(_x\)Cu\(_{1-x}\)Fe\(_2\)O\(_4\) nanocrystals at x=0, 0.1, 0.3, 0.5 and 0.7.

| Samples         | Saturation magnetization \( M_s \) (emu g\(^{-1}\)) | Coercivity \( H_c \) (Oe) | Remanent magnetization \( M_r \) (emu/g) | \( M_s / M_r \) | Magnetic moment \( \eta_B \) (\( \mu_B \)) | Magnetic anisotropy K (erg/g) |
|-----------------|-----------------------------------------------|-------------------------|-----------------------------------|--------------|-------------------------|---------------------------|
| Ni\(_x\)Cu\(_{1-x}\)Fe\(_2\)O\(_4\) | 16.97                                         | 341.29                  | 7.22                              | 0.425        | 0.727                   | 6033.01                   |
| Ni\(_{0.7}\)Cu\(_{0.3}\)Fe\(_2\)O\(_4\) | 24.01                                         | 419                     | 10.94                             | 0.456        | 1.026                   | 10479.36                  |
| Ni\(_{0.3}\)Cu\(_{0.7}\)Fe\(_2\)O\(_4\) | 27.78                                         | 86.02                   | 5.25                              | 0.189        | 1.183                   | 2489.20                   |
| Ni\(_{0.5}\)Cu\(_{0.5}\)Fe\(_2\)O\(_4\) | 35.09                                         | 144.00                  | 8.29                              | 0.236        | 1.488                   | 5263.5                    |
| Ni\(_{0.7}\)Cu\(_{0.3}\)Fe\(_2\)O\(_4\) | 39.29                                         | 133.88                  | 9.36                              | 0.238        | 1.663                   | 5493.26                   |

3.3. Dielectric properties and EM wave absorption properties

There are two fundamental parameters relative complex permittivity (\( \varepsilon = \varepsilon' - j\varepsilon'' \)) and magnetic permeability (\( \mu = \mu' - j\mu'' \)) corresponding to the reaction of materials to the incident EM wave. The \( \varepsilon' \) is the dielectric constant and \( \varepsilon'' \) is the dielectric loss. Figures 4(a) and (b) shows, \( \varepsilon' \) and \( \varepsilon'' \) variation respectively, with frequency for Ni\(_x\)Cu\(_{1-x}\)Fe\(_2\)O\(_4\). It was observed that \( \varepsilon' \) increases with the increase of frequency and decreases with the increase of frequency, which may be linked to the conducting networks conceived within the nano-particles and electronic polarization [48–50]. According to Koop’s theory, the decrease in \( \varepsilon' \) for an increase in frequency can be expressed by considering the solid as composed of well-conducting grains that are separated by poor conducting grain boundaries [51]. It is also observed that the \( \varepsilon' \) decreases with the increase in Ni content, which might be the reason for the substitution of Ni for Cu, modifying the structural homogeneity which attribute to the decrease in the degree of polarization. The value of \( \varepsilon'' \) is less than that of \( \varepsilon' \) and the variation of \( \varepsilon'' \) is non-linear with the frequency like \( \varepsilon' \), which may be due to the relaxation phenomenon of dipoles. The frequency dependence real part (\( \mu' \)) of permeability and the imaginary part (\( \mu'' \)) of permeability of nanocrystals are shown in figures 4(c) and (d). The resonance peaks appeared for the nanocrystals with different contents of Ni and showed a small upward shift in position with the increase of Ni content, which suggests the strong EM wave attenuation capacity. The dielectric loss tangents for complex permittivity and permeability are calculated by using the following equations (8) and (9) [52, 53]:

\[
\tan \delta' = \frac{\varepsilon''}{\varepsilon'}
\]

(8)

\[
\tan \delta'' = \frac{\mu''}{\mu'}
\]

(9)

To investigate the EM wave absorption properties, dielectric loss tangent (\( \tan \delta' \)), magnetic loss tangent (\( \tan \delta'' \)) and impedance matching (\( \left| \frac{Z}{Z_0} \right| \)) are the critical parameters for MW absorption materials. The values
of $\tan \delta_\varepsilon$ and $\tan \delta_\mu$, signifies the attenuation ability of dielectric and magnetic absorption materials. The MW impedance is used to analyze the impedance matching. Consequently, the values of $\tan \delta_\varepsilon$ and $\tan \delta_\mu$ should be as high as possible, though the MW impedance should be close to the impedance of free space to achieve zero reflection at the front surface of the material. The variation of $\tan \delta_\varepsilon$ and $\tan \delta_\mu$ for Ni$_x$Cu$_{1-x}$Fe$_2$O$_4$ nanoparticles with different Ni contents in the frequency range of 1-18 GHz can be observed in figures 4(e) and (f), respectively.

It can be observed, the values of dielectric loss tangents are low, and this low value might be because of the high density of the samples which attributed to the defect-free material. Figure 5(a) depicts the frequency-dependent impedance matching Ni$_x$Cu$_{1-x}$Fe$_2$O$_4$ nanocrystals. For the optimal impedance matching is equal or close to 1 indicates that the incident EM waves can totally enter into the inner of the absorption material, which is desired for an ideal EM wave absorption material. Hence, the Ni$_x$Cu$_{1-x}$Fe$_2$O$_4$ nanocrystals have a better
dielectric lossy capacity for EM wave. The values of tan δe and tan δm are the main factors determining EM wave attenuation, and are proportional to the dielectric and magnetic loss, respectively. Moreover, to further investigate the effect of Ni on the EM wave absorption properties of the NiₓCu₁₋ₓFe₂O₄ nanocrystals, the RL have been calculated by using the transmission line theory. According to transmission line theory, for a single layer absorption material with a backed metal plate, the RL values were simulated from the EM parameters by means of the following equations (10) and (11) [54–56]:

\[
R_L = 20 \log_{10} \left| \frac{Z_{in} - 1}{Z_{in} + 1} \right|
\]  

(10)

\[
Z_{in} = \sqrt{\frac{\mu}{\varepsilon}} \tanh \left[ j \frac{2 \pi f d}{c} \sqrt{\frac{\mu}{\varepsilon}} \right]
\]

(11)

where, 'Z_{in}' is input impedance, 'c' is the velocity of EM wave in free space, 'f' is frequency and 'd' is thickness. Figure 5(b) shows the RL values of all the samples with a thickness of 2mm in the frequency range of 1-18 GHz. The RL values for NiₓCu₁₋ₓFe₂O₄ nanocrystals show an absorption peak, shifting towards lower frequency with the increase of Ni content. Apparently, for an electric loss material, the value of complex permeability can affect the frequency of RL value. Hence, the increase in complex permeability attributed to the shifting of RL peaks to low frequency and the shifting distance is associated with the increasing rate of complex permeability. However, the RL values for all samples decreases with the increase in frequency. Among all the samples, NiₓCu₁₋ₓFe₂O₄ nanocrystals at x=0.1 possessed the lowest RL value i.e. −22.8 dB (RL ≤ −10 dB, absorption > 90%) at 16.09 GHz, indicates an optimal EM wave absorption performance, which might originate from the best relation between relative permittivity and permeability. Consequently, the as-prepared nanocrystals can perform better as EM wave absorber in P-band (12.4–18 GHz). Practically, an absorber with low thickness, wide bandwidth (RL ≤ −10 dB) and high RL is more desired. Hence, from the above results, it can be concluded that the NiₓCu₁₋ₓFe₂O₄ nanocrystals can be used to prepare high-performance EM wave absorption materials.

4. Conclusions

In summary, co-precipitation technique was used to synthesize a well cubic spinel structure of NiₓCu₁₋ₓFe₂O₄ nanocrystals. XRD and SEM results demonstrated that the as-prepared spinel phase nanocrystals are soft magnetic materials with potential usage in magnetic field sensing and information technologies. Magnetic properties showed that an increase in Ni content resulting in the increase of Ms. The ϵ decreases with the increase in frequency, though the ϵ″ increases with the increase in frequency, which may cause by the relaxation phenomenon of the dipole. The ϵ also decreases with the increasing content of Ni, which is the reason for decreasing crystallite size and highly dense nanocrystals. Though, the RL values for all ferrites descents with the increase in frequency. The lowest RL value −22.8 dB at 16.09 GHz (absorption > 90%) indicates an optimal EM wave absorption performance, which might originate from the best relation between relative permittivity and permeability. Consequently, the as-prepared nanocrystals can be used as the high-efficiency EM wave absorption materials.
Acknowledgments

The authors would like to extend their sincere appreciation to the financial supports from Inorganic Non-metal Institute of Shandong University, Shandong Provincial Science and Technology Department Project (No. 31370004011501) and Shandong Province Key research and Development Program (No. 2016ZDJ05A05) for its funding.

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