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Improved dielectric and magnetic properties of 1–3-type Ni₀.₅Zn₀.₅Fe₂O₄/epoxy composites for high-frequency applications

Li He¹, Haibo Yang², Di Zhou¹, Yujuan Niu¹, Feng Xiang¹ and Hong Wang¹,³

¹ Electronic Materials Research Laboratory, Key Laboratory of the Ministry of Education and International Center for Dielectric Research, Xi’an Jiaotong University, Xi’an 710049, People’s Republic of China
² School of Materials Science and Engineering, Shaanxi University of Science and Technology, Xi’an 710021, People’s Republic of China
E-mail: hwang@mail.xjtu.edu.cn

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Abstract
Ni₀.₅Zn₀.₅Fe₂O₄ (NZO)/epoxy composites with 1–3-type structure consisting of NZO rods in an epoxy matrix were fabricated by the dice and fill technique, with volume fraction from 40% to 70%. Improved frequency stability of the dielectric and magnetic properties was obtained in the frequency range from 10 MHz to 1 GHz. The optimized composite sample with 60% NZO rods in volume showed high dielectric and magnetic performance with permittivity between 9.2 and 10.3, dielectric loss between 0.09 and 0.25 in the frequency range from 50 MHz to 1 GHz, and permeability between 5.3 and 5.6, magnetic loss between 0.02 and 0.54 in the frequency range from 10 MHz to 1 GHz, respectively. Moreover, its permeability μ’ was increased to 170%, and the magnetic loss tan δµ was reduced to only 80% compared with the conventional 0–3-type composites with 40 vol% fillers at 1 GHz. The modelling and simulation results by Ansoft HFSS provided a reasonable explanation for the experimental results.

(Some figures may appear in colour only in the online journal)

1. Introduction

Soft magnetic materials are widely used in the electronic and information industry [1–4], especially in the design of miniaturized antennas [3–5] because of their high permittivity and permeability as well as low dielectric and magnetic loss tangents. However, conventional ceramic magnets can hardly meet the ever-growing demand for magnetic materials with better properties, especially for use at high frequencies. For example, the soft magnets of Ni–Zn ferrites possess very high permeability and low magnetic loss below the cut-off frequency, but their low cut-off frequencies (below 200 MHz) limit their applications in the high-frequency range of about 1 GHz [6–8].

In recent years, a dielectric–magnetic composite method has become increasingly popular and has been considered as an effective and feasible way to overcome the shortcomings of ferrites. Some previous studies [9–14] have focused on the improvement of the frequency stability of composite materials. One of the most common approaches is dispersing the ferrite powders into polymer matrices to form 0–3-type structure composites. Such 0–3-type structure composites have been studied and put into wide applications, and they play important roles in the structural design of magnetic composite materials [9–12]. Furthermore, some researchers have tried to study oriented composites by introducing an external magnetic field to the 0–3-type composites during the moulding process, and the oriented composite always shows better properties than the unoriented one [11, 12].
However, the 0–3-type composite has some intrinsic drawbacks. For example, the permeability and saturation magnetization of the 0–3-type composite are low because the volume fraction of the ceramic filler is always less than 50% to ensure the mechanical strength of the composites. Several researchers have reported their interesting findings on 2–2-type structure magneto-dielectric composites [13, 14], which possess lower magnetic loss compared with a 0–3-type composite. Yet, the permeability of the 2–2-type composite was still low, and the research
results indicated that a suitable selection of the composite structure can help in improving the magnetic properties of the composites.

In this study, a kind of dielectric–magnetic composite with 1–3-type structure is obtained by introducing oriented Ni$_0$Zn$_{0.5}$Fe$_2$O$_4$ (NZO) rods into an epoxy matrix. The fabrication method, frequency dependence of the magnetic and dielectric properties, as well as a comparison with conventional 0–3-type composites, and the modelling and simulation analysis of the composite are reported and investigated.

2. Experiment

NZO ceramic bulks were synthesized via the conventional solid-state reaction method and sintered at 1300 °C for 3 h. X-ray diffraction was performed by x-ray diffractometry with Cu Kα radiation (D/MAX-2400 x-ray diffractometer, Rigaku, Tokyo, Japan) to confirm that the pure phase of NZO ceramic is obtained. The microstructure of the NZO ceramic observed by a scanning electron microscope (JSM-6460, JEOL, Tokyo, Japan) is dense and uniform (figure 1(a)).

The fabrication process of the 1–3-type NZO/epoxy composite by the dice and fill technique [15–17] is shown in figure 1. The as-sintered NZO ceramic ring is displayed in figure 1(a). The ring sample was then diced to a rod array by a computer-programmed diamond saw. First, a series of parallel cuts were made in the NZO ceramic. Then, the sample was rotated 90° and a second series of perpendicular cuts were made. During this step, the total volume fraction of NZO in the 1–3-type composites could be designed by adjusting the width of the NZO rods. When the cutting width was fixed at 0.35 mm (the blade thickness), the volume fraction of NZO was controlled at about 40%, 50%, 60% and 70%, with different widths of the NZO rods at 0.6 mm, 0.9 mm, 1.2 mm and 1.8 mm, respectively. Therefore, a NZO rod array with ceramic base was obtained, as shown in figures 1(b) and (c). Then, the NZO rod array with the ceramic base was placed in a pre-prepared silicone rubber mould and the liquid epoxy solution (resin: diglycidyl ether of bisphenol A (DGEBA), hardener: methyl tetrahydrophthalic anhydride (MTHPA), ratio= 1:1, curing temperature 150 °C for 12 h, Nantong Stars Synthetic Material Co., LTD, China) was infiltrated into the sample in vacuum to bond the pillars. The sample was then solidified at the curing temperature until the curing process was over (figure 1(d)). After that, the 1–3-type composite was cut into flakes with a thickness of about 2 mm, as shown in figure 1(e). Figure 1(f) shows the top view of the actual sample of the 1–3-type NZO/epoxy composite, of which the structure of the 1–3-type composite is dense and uniform.

For comparison and contrast, 0–3-type composite samples were also prepared. The calcined and ball-milled NZO powders were annealed at 1100 °C for 3 h in order to get magnetic fillers. And epoxy was used as the dielectric matrix of the composites. They were fully mixed together with a volume fraction of 40% to form well-dispersed 0–3-type composites. The mixture was placed in the pre-prepared annular groove silicone rubber mould ($d_{out} = 15$ mm, $d_{in} = 9$ mm, $h = 2$ mm) to pump air into the vacuum state for 2 h and then solidified in open air at the curing temperature (150 °C) for 12 h.

Magnetic and dielectric measurements of the composites in the frequency range 10 MHz–1 GHz were carried out by an impedance analyser (4291B Hewlett Packard, Palo Alto, CA) with a 16454L magnetic material test fixture and a 16453A dielectric material test fixture, respectively. The magnetic hysteresis loops of the composite were measured in two different directions of the magnetic field, both horizontal and vertical, by a vibrating sample magnetometer (VSM) (Lake Shore 7410, Westerville, OH). The models of the 0–3- and 1–3-type composites were also established, and their simulation results were obtained by Ansoft HFSS.

3. Results and discussion

Figure 2 shows the magnetic hysteresis loops of the NZO/epoxy 1–3-type structure composites with different volume fractions of oriented NZO rods. It is observed that the saturation magnetization ($M_s$) increases with the increase in the concentration of the NZO rods, since the magnetic properties of the composite are significantly influenced by the total content of the magnetic material. When the concentration of NZO rods is 70%, $M_s$ is 69.5 emu g$^{-1}$, which is about 86.7% of the $M_s$ (80.2 emu g$^{-1}$) of the Ni$_0$Zn$_{0.5}$Fe$_2$O$_4$ ferrite ceramics sintered at 1300 °C.

Figure 3 shows the magnetic hysteresis loops in the magnetic field ranges ($a$)−10 000 to 10 000 Oe and ($b$)−20 to 20 Oe of the 1–3-type structure NZO/epoxy composite with a volume fraction of 50%. The samples were measured in two different directions of the magnetic field, horizontal ($H_x$) and vertical ($H_z$), as shown in the inset of figure 3(a). It is observed that the slope of the hysteresis loop ($\alpha = dM/dH$) and the coercivity ($H_c$) all decrease if the test direction of the magnetic field is adjusted from the horizontal to the vertical direction. According to the shape anisotropy, increasing ferrite units along the horizontal direction make it an easier magnetization
Figure 3. Magnetic hysteresis loops in the magnetic field ranges (a) −10 000 to 10 000 Oe and (b) −20 to 20 Oe of the 1–3-type structure NZO/epoxy composite with 50% volume fraction of NZO rods. Each sample is measured in two different directions of the magnetic field, horizontal direction ($H_1$) and vertical direction ($H_2$), as shown in the inset of (a).

Table 1. Comparison of the effective magnetic and dielectric properties of the 1–3- and 0–3-type NZO/epoxy composite structures at 1 GHz.

<table>
<thead>
<tr>
<th>NZO (vol%)</th>
<th>$\mu'$</th>
<th>$\tan \delta_\mu$</th>
<th>$\varepsilon'$</th>
<th>$\tan \delta_\varepsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rods</td>
<td>40</td>
<td>2.27</td>
<td>0.16</td>
<td>7.27</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>3.73</td>
<td>0.35</td>
<td>8.76</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>5.37</td>
<td>0.55</td>
<td>9.676</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>6.18</td>
<td>0.90</td>
<td>10.89</td>
</tr>
<tr>
<td>Powders</td>
<td>40</td>
<td>3.13</td>
<td>0.67</td>
<td>5.97</td>
</tr>
</tbody>
</table>

The frequency dependence of the magnetic properties of the 1–3-type NZO/epoxy composite with different volume fractions of NZO rods is shown in figure 4. It can be seen that the initial permeability and magnetic loss of the composite increase slightly with the increase in the volume fraction of NZO rods. Meanwhile, when the volume fraction of NZO rods is not more than 60%, each curve shows perfect frequency stability and relatively low magnetic loss within 1 GHz.

Figure 4. Frequency dependence of the magnetic properties of the 1–3-type structure NZO/epoxy composites and the 0–3-type NZO/epoxy composite which is used for comparison. Direction, which leads to a larger slope for the hysteresis loop. However, the periodical cuts increase the separation between the magnetic grains and units, thereby enhancing the coercivity ($H_c$).
Figure 5. Simulation results of the transmission of electromagnetic energy in the sintered NZO ceramic bulk and its derived composite. The volume fraction of NZO ferrite in the composites is set to be 50%.

particles dispersed uniformly in the epoxy matrix and each of them worked as a miniature NZO bulk unit as the one shown in figure 5(a), and the particles together led to a relatively large electromagnetic energy loss.

However, in the 1–3-type NZO/epoxy composite, if the incident direction of the electromagnetic wave is parallel to the NZO rod array, the electromagnetic energy would be focused in the cuts filled with epoxy around the oriented NZO rods (figure 5(d)). This indicates that the oriented low-loss polymer material, along the propagation direction of the electromagnetic wave, provides an oriented low-loss region for the transfer of electromagnetic energy inside the magnetic composite, and finally decreases the overall magnetic loss of the composite material in such a structure.

The good frequency stability of \( \mu' \) for the composite with 1–3-type structures can be understood based on the following Maxwell–Garnett mixing law:

\[
\mu' = \frac{(\mu_b - 1)p}{(\mu_b - 1)(1 - p)N_d + 1} + 1,
\]

where \( N_d \) is the demagnetizing factor of the fillers, \( p \) is the volume fraction and \( \mu_b \) is the static real permeability of the bulk material [20, 21]. This shows that \( \mu' \) of the composites is closely related to \( N_d \). A large \( N_d \) leads to a small \( \mu' \), if the permeability of bulk materials, \( \mu_b \), is the same.

In the 1–3-type structure composite, with the increase in the filler concentration, the ratio of the thickness to average length (aspect ratio) of the NZO rods is reduced due to the limitation of unchanged blade thickness. So it is true that the composite with 40% NZO rods has a larger demagnetizing factor \( N_d \) and a lower volume fraction, which lead to its smaller \( \mu' \) and hence result in a better high frequency stability according to Snoek’s law [10].
According to the Maxwell–Garnett mixing law, the dependence of \( \mu' \) on \( p \) and \( N_d \) is fitted, as shown in figure 6. The values of calculated \( N_d \) and the fitted curves prove that the above analysis is valid. \( N_d \) decreases from 0.58 to 0.28 with the decrease in the aspect ratio of the NZO rods.

The fit curves and the above analysis both indicate that the aspect ratio of NZO rods in the 1–3-type structure can be designed to obtain composites with different \( N_d \) in order to improve the magnetic frequency properties of the composite. The experimental results confirmed that the 1–3-type samples with a larger \( N_d \) show better frequency stability of permeability up to 1 GHz. Meanwhile, a sample with higher volume fraction has higher permeability and larger magnetization saturation. So it can be inferred that a 1–3-type structure sample with both larger \( N_d \) and higher volume fraction, such as the model sample shown in the inset of figure 6, might have a larger magnetization saturation, higher permeability, lower magnetic loss and better frequency stability. However, this corollary has not yet been verified due to the limited experimental conditions.

The dielectric properties of the 1–3-type NZO/epoxy composite in the frequency range from 50 MHz to 1 GHz are shown in figure 7. The permittivity of the 1–3-type structure composite can be predicted by a simple parallel capacitance model and expressed as

\[
\varepsilon_c = \varepsilon_{NZO} \times p + \varepsilon_e \times (1-p),
\]

where \( \varepsilon_c, \varepsilon_{NZO} \) and \( \varepsilon_e \) are the permittivities of the composite, NZO and epoxy, respectively; \( p \) is the volume fraction of NZO [22–24].

It can be seen in figure 8 that the permittivities of the composite increase linearly with the increase in the volume fraction of NZO rods, and the curve fitting is in good agreement with the experimental data. The dielectric loss of the composite displays no marked difference with the change in volume fraction, which may be caused by the structural characteristics of the 1–3-type composite. As shown in figure 5(d) in the 1–3-type composite, the electromagnetic wave propagated mainly along the oriented low-loss region provided by the epoxy filling in the cuts between the NZO rods. The experimental results show that the dielectric–magnetic composite with 1–3-type structure exhibits good frequency stability and a relatively low dielectric loss in the frequency range from 10 MHz to 1 GHz.

### 4. Conclusion

Dielectric–magnetic composites with high filler concentration, good frequency stability and relatively low loss can be achieved by the 1–3-type structure design even if the initial filler material shows significant loss values. The relative permeability of the composite with \( f_{NZO} = 60 \text{ vol}\% \) remains stable between 5.3 and 5.6 from 10 MHz to 1 GHz, and a low magnetic loss is achieved.

Moreover, its permeability \( \mu' \) is increased to 170% and the magnetic loss \( \tan \delta_\mu \) is reduced to only 80%, as compared with the conventional 0–3-type composites with 40 vol% fillers. The simulation results show that the remarkably enhanced magnetic properties are due to the oriented low-loss region along the electromagnetic wave propagating direction provided by the low-loss epoxy filling in the cuts between the NZO rods.

From the results and the above analysis, it can be concluded that in the design of dielectric–magnetic composites, the structure type, the demagnetizing factor of the fillers (\( N_d \)) and the volume fraction should all
be taken into account. The prominent advantage of the composites is that the cut-off frequencies of the composites are higher than 1 GHz when the volume fraction of NZO is not more than 60%. The sample with 60% NZO is the optimal composite with optimized comprehensive properties of permeability, magnetization saturation and magnetic loss tangent. Compared with the conventional 0–3-type composite, this kind of 1–3-type dielectric–magnetic composite possesses higher permeability, larger magnetization saturation, lower magnetic loss and better frequency stability from 10 MHz to 1 GHz for potential high-frequency applications.

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