



# Microwave sintering carbon nanotube/ $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ composites and their electromagnetic performance

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## Abstract

Carbon nanotube (CNT)– $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$  powders were prepared by *in situ* chemical precipitation and hydrothermal processing, and further sintered by microwave sintering technology. The results show that CNTs acted as ‘heating source’ and promoted the consolidation of composites during the microwave sintering process. However, too much CNTs (such as 5 wt%) led to phase decomposition and reduction of ferrite materials because of the ultra-high localized temperature building up in the interface of CNTs and ferrite grains. The electrical conductivity of composites increased by more than seven orders of magnitude when compared to that of pure  $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ , and remained a high value at the temperature of 70 K (for example, 1 wt% CNT/ $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$  sample kept conductivity of 0.1 S/m). The saturation magnetization was strongly dependent on the mass percentage of CNTs. With the increase in CNT content, both the real and the imaginary permittivity were increased in the frequency region 0.6–5 GHz (L and S bands). According to the measured results of  $\epsilon_r$  and  $\mu_r$ , the frequency-dependent reflectance loss (RL) of CNT/ $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$  composite ceramics with different CNT content was evaluated. The CNT-doped ferrite ceramics discussed herein is very promising to be used in an on-beam-line high-order mode (HOM) load in particle accelerators based on superconducting RF due to their excellent low-temperature characteristics.

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**Keywords:** Ferrite; Carbon nanotube; Electromagnetic property; Microwave sintering

## 1. Introduction

Ni–Zn ferrites have been intensively studied due to their high resistivity, low dielectric losses, high Curie temperature and excellent microwave-absorbing properties,<sup>1–3</sup> and have widely employed in both low and high frequency devices that play a key role in many technological applications, such as microwave equipments, power transformers in electronics, rod antennas and read/write heads for high speed digital tape, etc.<sup>4–7</sup> One of the most demanding applications for the ferrite materials in advanced particle accelerators based on superconducting RF is to serve as microwave absorber or an on-beam-line higher-order mode (HOM) load. The microwave absorber in such a device

must meet some requirements, such as chemical and physical stability at cryogenic temperatures, appropriate DC electrical conductivity for charge drainage, low vacuum out-gassing rate, radiation tolerance, good thermal conductivity and wide-range-bandwidth microwave absorption. However, ferrites normally exhibit dramatic reduction in DC conductivity at low temperatures (liquid-nitrogen temperature), making them unsuitable for charge drainage.

One solution for this shortage of ferrite materials is to incorporate conductive filler to form a conduction network. One-dimensional carbon nanotubes (CNTs) possess remarkable mechanical, thermal, and electrical properties, which have been used to form conductive network in various composites.<sup>8,9</sup> Since their discovery by Iijima in 1991,<sup>10</sup> they have been triggered a worldwide research efforts. Theoretical and experimental results showed that CNTs have superior electrical property and their electric-current carrying capacity is 1000 times higher than that

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of copper wires.<sup>11</sup> When CNTs were incorporated into NiFe<sub>2</sub>O<sub>4</sub> ferrite, the electrical conductivity of composite increased by 5 orders of magnitude at room temperature after addition of 10 wt% CNTs<sup>12</sup>. Considering the outstanding electronic property of CNTs as well as microwave absorption property of Ni–Zn ferrite nanoparticles, CNT/Ni–Zn ferrite composites would be very attractive for practical applications that need comprehensive physical properties.<sup>13–16</sup> But most of previous investigations focused on the synthesis of composite powders, few reports concerned on the sintered bulk materials and their electromagnetic properties. Moreover, there are few attempts to fabricate ferrite ceramics through self-heating using microwave sintering technique although this kind of materials can efficiently absorb microwave energy. Since microwave sintering technique can transfer power energy into heat within the volume of sample, a homogeneous sintering process can be achieved in much short time.<sup>17,18</sup> It has been observed that microwave-sintering technique can efficiently reduce the grain growth and enhance the densification rate of ceramics.<sup>19–21</sup> Therefore, this technique is expected to lower the sintering temperature and shorten the annealing time when it is employed to fabricate CNT/Ni–Zn ferrite composites since two inclusive components have good microwave absorbing property.<sup>22</sup>

In this study, a co-precipitation hydrothermal method was used to prepare ferrite-nanoparticle-attached CNTs which were well dispersed into spontaneously-formed ferrite suspension. Furthermore, the as-prepared CNT/Ni<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub> blends with different content of CNTs were sintered by microwave sintering technology. The electrical conductivity of composite ceramics was measured at temperature ranging from 70 K to 300 K, and their microwave reflection loss feature was determined by measuring complex permeability and complex permittivity. A specific attention was paid on the effect of the CNT contents on the electromagnetic properties of the bulk materials.

## 2. Experimental details

Multiwalled carbon nanotubes (diameters: 50–60 nm, length: 2–10 μm, purity: 95%) were purchased from ShenZhen Nanoport Ltd. Co. (China). CNTs were first oxidized by refluxing at 150 °C in concentrated nitric acid for 5 h. After the solution was cooled to room temperature, the oxidized CNTs were separated by filtration using a 0.22 μm filter membrane and repeated washing with distilled water, and then mixed with sodium lignosulfonate (SLS) in 500 ml distilled water followed by ultrasonication treatment for 45 min. The SLS-functionalized CNTs were separated out by filtration and the excessive SLS was removed by repeated rinsing with distilled water. The obtained SLS-functionalized CNTs were well dispersed and stored in deionized water. Afterward, the CNT suspension was mixed with solution containing Ni(NO<sub>3</sub>)<sub>2</sub>, Zn(NO<sub>3</sub>)<sub>2</sub> and Fe(NO<sub>3</sub>)<sub>3</sub> with the Ni:Zn:Fe molar ratio of 0.5:0.5:2. Then the above mixture solution was dropwise added into NaOH solution under vigorous stirring until the pH value reached 10.5. The mixture was stirred for extra 1 h for complete reaction. The as-received precursor was then placed in a Teflon-lined autoclave and hydrothermally

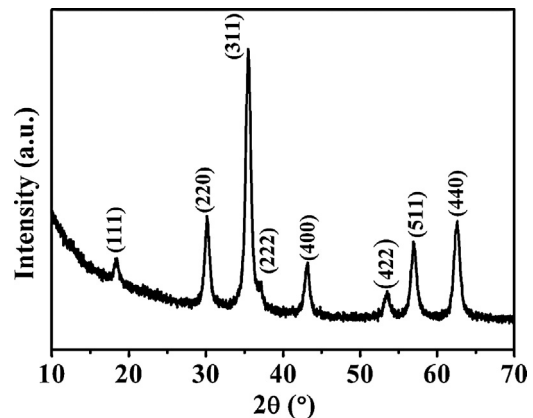


Fig. 1. X-ray diffraction pattern of 2 wt% CNT/Ni<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub> composites hydrothermally treated at 200 °C for 3 h.

treated at 200 °C for 3 h. The finally obtained precipitates were then washed repeatedly with deionized water, and further dried at 80 °C for 5 h.

The composite powders were cold pressed into φ20\*3 mm<sup>3</sup> pellets, and then consolidated by microwave sintering (MWS) technology at 1000 °C for 1 h in N<sub>2</sub> atmosphere using the HAMiLab-HV3 Type microwave sintering furnace (Synotherm corporation, China). Density of the sintered composites was measured using the Archimedes technique. The electrical conductivity and saturation magnetization of the composites were measured by physical properties measurement system (PPMS, Quantum Design, USA). The geometry of samples for microwave measurements using an Agilent 8722 vector network analyzer is toroidal ring with the inner diameter of 3 mm and the outer diameter of 7 mm. The frequency range selected for microwave measurements is 0.6–5 GHz.

XRD patterns of the composites were collected by powder X-ray diffraction (XRD, Bruker AXS D8 Discover, Germany), using Cu Kα radiation. Morphology analysis of the composites was characterized by a scan electron microscopy (SEM, Hitachi S-4800, Japan) equipped with an energy dispersive spectroscopy (EDS) system. Transmission electron microscopy (TEM, Tecnai F20, Phillip, Holland) was applied to observe the microstructure of the composites.

## 3. Results and discussion

The typical XRD pattern of 2 wt% CNT/Ni<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub> composite powder that hydrothermally treated at 200 °C for 3 h is shown in Fig. 1. The characteristic diffraction peaks are well consistent with that of the standard JCPDS card No. 8-234, indicating the product is a pure spinel phase. The characteristic peak at 26.24° that corresponds to CNTs cannot be found in this XRD pattern which may due to the low content of CNTs or full coverage of ferrite nanocrystals on the CNTs (Fig. 2a). Moreover, no diffraction peak due to any other new phase is observed, which indicates the incorporation of CNTs had no impact on the formation of designed ferrite phase. The average grain size of ferrite calculated by Scherrer formula is about 20 nm.

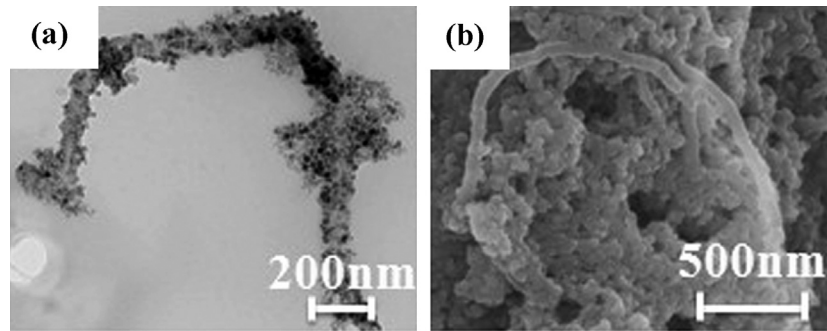


Fig. 2. TEM (a) and SEM (b) images of 2 wt% CNTs/ $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$  composites hydrothermal treated at 200 °C for 3 h.

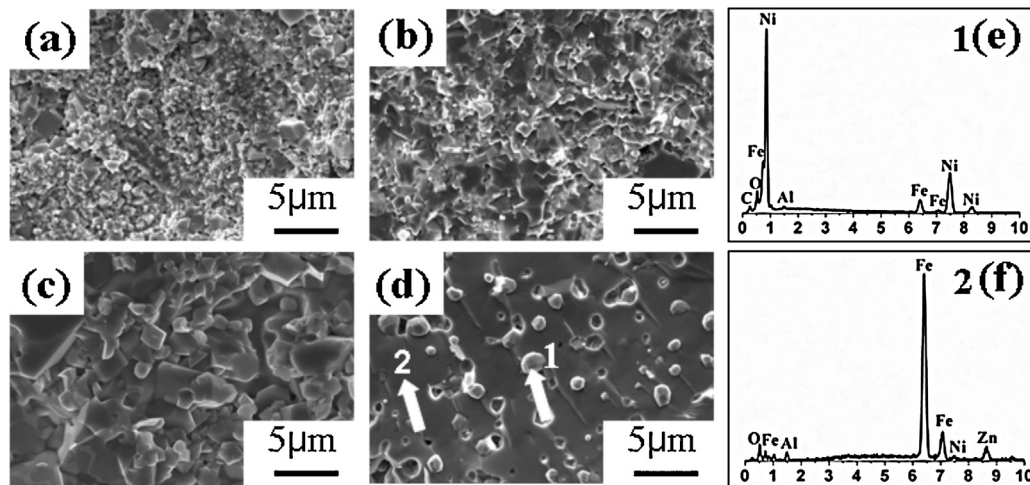


Fig. 3. SEM images of the fracture surface of samples that sintered at 1000 °C for 1 h: (a) pure ferrite, (b) 1 wt% composite, (c) 2 wt% composite, and (d) 5 wt% composite. EDS spectra of area 1 (e) and 2 (f) arrowed in the (d).

Fig. 2 presents the representative TEM and SEM images of CNT/ $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$  composite powder with 2 wt% CNTs, respectively. It can be seen that CNTs are well distinguished and retain the original structure in the composite powder. A thick layer of ferrite nanocrystals well coated on the out wall of one carbon nanotube (Fig. 2a). The as-formed nanoparticle-attached carbon nanotubes favored the final dispersion of CNTs in solution as well as in the matrix materials (Fig. 2b). The reason for such effect can be understood as high density of hydrophilic groups (such as hydroxyl and sulfonate ones) is grafted on the carbon nanotubes surface after combined surface treatment of covalent (reflux in concentrated nitric acid) and non-covalent functionalization (interaction with SLS molecules). The zeta potential value of surface-negative-charged CNTs maintained about  $-50$  mV at pH of 10.5, which afforded a suitable surface environment for in-site nucleation and growth of  $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$  nanocrystals through charge attraction with cations.<sup>23</sup>

Morphologies of fracture surfaces of sintered bulks with different CNT content are shown in Fig. 3(a–d). All samples were fabricated by microwave sintering at 1000 °C for 1 h. Compared with the sample without CNTs (Fig. 3a), the samples with 1 wt%, 2 wt% and 5 wt% CNTs have higher density (Table 1), indicating the enhanced sintering behavior in the composites containing carbon nanotubes. High density of composite

ceramics benefits the application as HOM load that needs low out-gassing rate. Furthermore, there are some newly formed ball-like grains embedded in the ferrite grain when CNT content is high (Fig. 3c), and these tiny grains become more prominent in the 5 wt% sample (Fig. 3d). The diameter of the ball is about 1–2  $\mu\text{m}$ . In order to confirm the chemical composition of ball-like phase, EDS analysis was carried out. According to the EDS analysis of area marked ‘1’ in Fig. 3d, the ball-like precipitate was mainly composed Ni and Fe (Fig. 3e). The atomic ratios of the elements reveal that the precipitate mainly contains  $\text{FeNi}_3$  which was also consistent with the further phase identification by XRD technique (Fig. 4). The Ni and Fe element are believed

Table 1  
Physical property of CNTs– $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$  composites fabricated by MWS at 1000 °C for 60 min.

CNTs contents	Density ( $\text{g}/\text{cm}^3$ )	$M_s$ (emu/g)	$\sigma$ (S/m)	
			300 K	70 K
CNTs-free	4.89	76.99	$4.54 \times 10^{-6}$	N/A
0.5 wt%	4.96	71.56	0.37	N/A
1 wt%	5.12	81	140.33	0.1
2 wt%	5.23	86.6	2.75	0.004
5 wt%	5.45	20.15	1.21	0.003

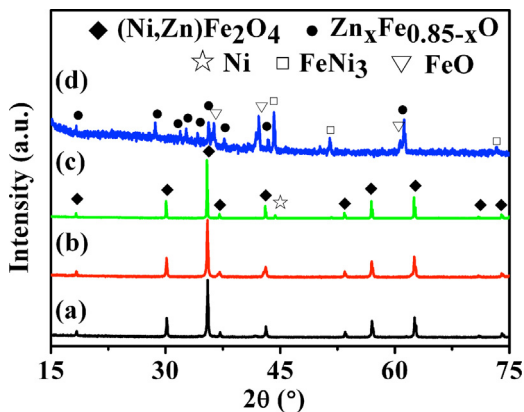


Fig. 4. XRD patterns of  $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$  ferrites samples containing (a) 0 wt% CNTs; (b) 1 wt%; (c) 2 wt% and (d) 5 wt% CNTs that microwave sintered at  $1000^\circ\text{C}$  for 1 h.

released from ferrite to form  $\text{FeNi}_3$ . Meanwhile, this decomposition process also led to formation of other new phase, such as  $\text{Zn}_x\text{Fe}_{0.85-x}\text{O}$  that can be confirmed by EDS (Fig. 3f) and XRD (Fig. 4d) analysis. It is interesting to note that the nickel atom locating at ‘A’ site in the ferrite crystal should firstly be reduced and then the iron atom at ‘B’ site, showing the bonding strength of different element in the ferrite crystal.

It is worthy noting that at the same sintering condition the composite ceramics fabricated by conventional heating method (such as in tube furnace) the products were composed of CNTs and basic ferrite without any other new phase. As one of main characteristics of microwave heating method, the local temperature in the sintered bulk depends on the physical property (dielectric, magnetic and conductive features) of local material composition. Considering the multiple interaction of electromagnetic wave with matter at the interface of the CNT and ferrite grain, the capability of microwave absorption at this location will be largely enhanced. Thus, the temperature increased quickly near CNT ‘susceptor’ in the bulk material and was far higher than the temperature on the up surface of bulk monitored by a remote pyrometer. The local high temperature condition led to the decomposition and reduction of ferrite to form metals (or alloys) and other phases. It is of evidence that the higher content of CNT in the composite the more ferrite materials would be reduced. In fact, trace of Ni metal ‘dots’ can be observed in the SEM image (Fig. 3c) and was also identified by XRD result (Fig. 4c) in the microwave-sintered 2 wt% composite. At high doping level such as 5 wt% CNT, additional phases including ferrous oxide,  $\text{FeNi}_3$  alloy and Fe-scarce  $\text{Zn}_x\text{Fe}_{0.85-x}\text{O}$  ferrite existed in the product due to decomposition of  $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$  phase and reduction by carbon at high temperature (Fig. 4d). The local overheating effect during microwave sintering was not only reflected by the decomposition of ferrite material and reduction of magnetic particles (Fe and Ni), but was also easily observed by the microstructure change. Obviously, the dimensions of ferrite grains in the CNT-doped samples were larger than that of blank one (Fig. 3a–c). The element diffusion (surface or volume diffusion) was accelerated a lot especially near the interface of CNT and grain where much high temperature can be achieved due to efficient microwave absorption.

Meanwhile, the formation of liquid Ni metal and Ni–Fe alloy through reduction of ferrite at high temperature also acted as sintering aids and promoted the grain boundary movement of ferrite. Combining these factors, the grain growth kinetics was considerably accelerated as proved by microstructure evolution (Fig. 3a–d).

In the microwave field, the self-heating capability of a material is determined by its dielectric loss tangent:  $\tan \delta = \varepsilon''/\varepsilon'$ , where  $\varepsilon'$  and  $\varepsilon''$  represent the real and imaginary permittivity of complex permittivity, respectively. Menéndez et al.<sup>24</sup> and Zhang and Zhu<sup>25</sup> reported the dielectric loss tangent of carbon nanotubes is 0.25–1.14 at the frequency of 2.45 GHz at room temperature, while the dielectric loss tangent of  $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$  is only 0.01–0.02 as Peng<sup>26</sup> and Cho et al.<sup>5</sup> investigated. Furthermore, carbon nanotubes possess huge surface area and a large number of dangling bonds, which strengthens the absorbing properties for interfacial polarization and multiple scattering effects. In addition, carbon nanotubes also have good electrical conductivity. Thus, conductance loss is also one of important contributions to its good microwave absorbing property<sup>27</sup>. In CNT/ $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$  composites, the presence of a larger number of CNT/ $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$  interfaces gives rise to enhanced interfacial polarization effect. Interfacial polarization aided the microwave absorption due to the interaction of electromagnetic wave with charge multipoles at the interface<sup>28</sup>. Therefore, during microwave heating processing, the location around CNTs was heated far more rapidly than  $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$  grain itself, and acted as a ‘heating source.’ The density of these ‘heating sources’ is dependent on the dispersion and concentration of CNTs. Also, the heat generated by microwave power conversion builds up more quickly if the matrix material is a thermal insulator (low thermal conductivity). Therefore, a big temperature gradient will exist at the grain boundary or in the interface of CNT and ferrite, which is the driving force for the  $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$  grain growth. In the extreme condition the over-high temperature surrounding CNTs leads to decomposition of  $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$  and following reduction of oxide materials (as indicated in the 2 wt% and 5 wt% samples). The above results is meaningful to guide the composite fabrication by microwave sintering that too much CNT addition will lead to phase decomposition and microstructure alternation that is unexpected in the samples by conventional heating approach.

Fig. 5 is the hysteresis loop of CNT/ $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$  bulks. All exhibit typical soft ferrite behavior. The residual magnetization and coercive force are nearly zero. With the increment of carbon nanotubes contents, saturation magnetization of the composites increased a little in 1 wt% and 2 wt% samples but decreased a lot in 5 wt% sample. Compared with the pure  $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ , the lower saturation magnetization of the 0.5 wt% CNTs– $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$  is due to the doping of the nonmagnetic substance of CNTs, but the higher saturation magnetization of 1 wt% CNTs and 2 wt% CNTs composites is due to increased grain size and volume density. While the drastically devastation of saturation magnetization in the sample of 5 wt% CNT/ $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$  is due to the decomposition of  $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$  as discussed in the phase characterization section.



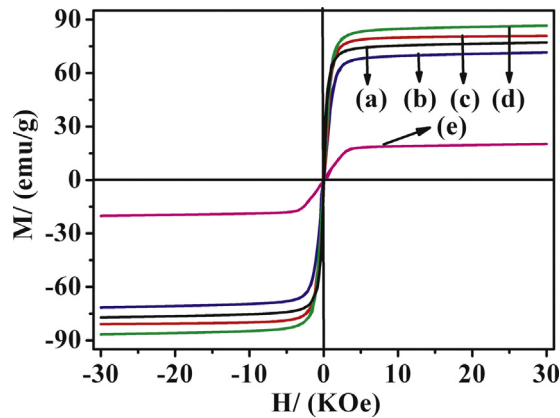


Fig. 5. Hysteresis loops of composites with different CNTs contents: (a) 0 wt%; (b) 0.5 wt%; (c) 1 wt%; (d) 2 wt%, and (e) 5 wt%.

Temperature-dependence of electrical conductivity of CNT/Ni<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub> composites with different CNT content shows much improvement in the conductivity in a wide temperature range (Fig. 6). It can be seen that the pure Ni<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub> exhibits typical insulator properties and the electrical conductivity is only  $4.54 \times 10^{-6}$  S/m at room temperature. With the CNTs addition, the electrical conductivity significantly increased. The electrical conductivity of 1 wt% composite achieved the maximum value of 140.33 S/m at room temperature in all samples observed, and the electrical conductivity gradually decreased as the temperature decreased that was the characteristic semiconductor behavior. Even though the temperature dropped to the liquid helium temperature of 70 K, the electrical conductivity of 1 wt% composite remained at 0.1 S/m. There have been widely reported that the addition of CNTs can effectively improve electrical conductivity of structural ceramics in which the metallic or semiconducting CNTs that depending on the chirality of the CNTs formed three-dimensional conductive network along grain boundary<sup>29–32</sup>. The large aspect ratio of CNTs resulted in an entangled network of conductive pathways in the ceramic composites at a much low threshold value, so the electrical conductivity increased significantly in

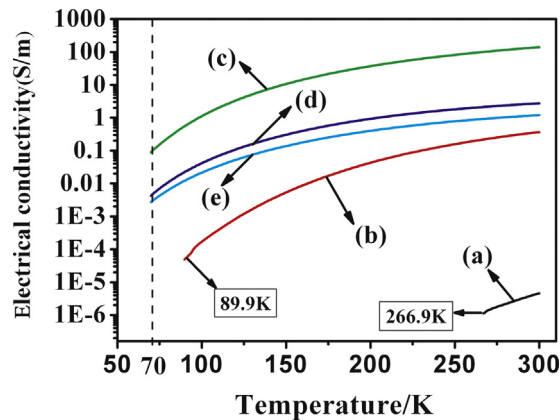


Fig. 6. Temperature dependence of electrical conductivity of CNT/Ni<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub> composites with different CNTs contents fabricated by microwave sintering method at 1000 °C for 1 h: (a) 0 wt%, (b) 0.5 wt%, (c) 1 wt%, (d) 2 wt%, and (e) 5 wt%.

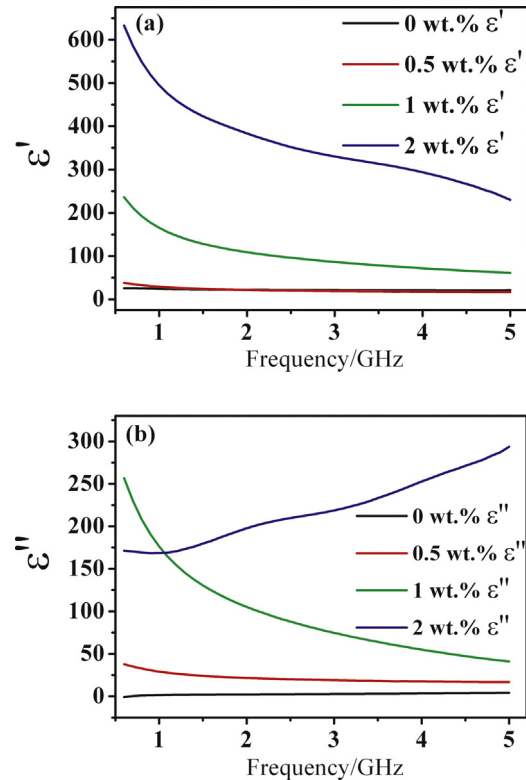


Fig. 7. Complex permittivity of CNT/Ni<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub> composites: (a) the real permittivity and (b) the imaginary permittivity.

the 1 wt% CNT/Ni<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub> composites. However, in the higher content of CNTs, the unexpected decomposition of ferrite and the following reduction reaction during microwave sintering consumed much of CNTs (Figs. 3c–d), leading to destroy of conductive network. Therefore, the electrical conductivity of 2 wt% and 5 wt% composites were lower than that of 1 wt% composite that is contrary to the results in previous work in which conductivity of composites monotonically increased as the CNTs increased. The lowered resistivity of ferrite at low temperature will benefit the charge drainage when it is used as on-beam-line higher-order mode (HOM) load in the accelerator as discussed in the introduction.

Fig. 7 shows the complex permittivity of CNTs–Ni<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub> composites with different CNTs contents sintered via microwave sintering method at 1000 °C for 1 h. With the increment of CNTs content, both the real and the imaginary permittivity increase. A small amount addition of CNTs (0.5 wt%) into Ni<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub> did not noticeably change the real permittivity but the imaginary part value multiplied more than five times (Fig. 7). When the CNTs contents rose to 1 wt% and 2 wt%, the real part of permittivity at frequency of 0.6 GHz increases rapidly to 250 and 165, respectively. A similar phenomenon has been widely reported in the carbon nanotube composite system.<sup>12,16,29,33</sup> Ghasemi et al. regarded the increase of permittivity was primarily attributed to the improvement of conductivity by CNTs<sup>34</sup>. CNTs with excellent electrical conductivity and high aspect ratio can easily form conducting network within the ferrite matrix. The conducting networks would interact and attenuate the electromagnetic wave effectively. Song

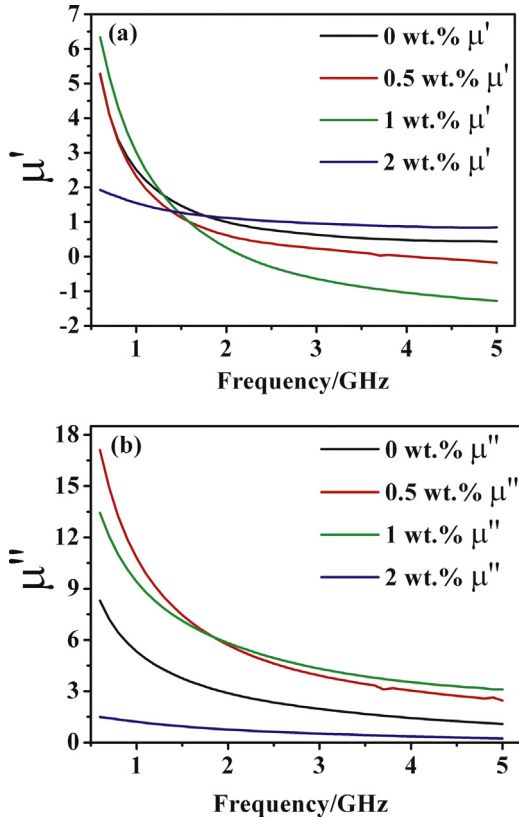


Fig. 8. Complex permeability of CNTs–Ni<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub> composites: (a) the real part and (b) the imaginary part.

et al.<sup>35</sup> and Ahmad et al.<sup>36</sup> thought it was because the conductive network formed by CNTs in composite could be seen as mini capacitors. The polarization effects between which improves the charge storage capacity and the real part of permittivity of composite. As to the increase of the imaginary part of the permittivity, it could be attributed to the increase in electrical conductivity loss in the composites<sup>16,27</sup>. For the specific application in the HOM load device, the microwave attenuation capability is determined by the imaginary part of permittivity but also relates to the real part which tells how much microwave power penetrates into absorber material. In the composites containing CNTs more than 1 wt%, the real part augment too much, meaning much of microwave power will be scattering from the surface of materials.

Fig. 8a and b shows the real and imaginary part of the permeability of CNT/Ni<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub> composites sintered by microwave at 1000 °C for 1 h, respectively. When the CNTs content is lower than 1 wt%, the real and imaginary parts of permeability of composites decreases rapidly with increasing frequency at the range of 0.6 GHz–2 GHz, finally becomes relatively flat with frequency range of 2–5 GHz. For the sample of 2 wt% CNTs, the real part of permeability is lower than that of other samples in the range of 0.6–1.5 GHz, while similar to other samples at 2–5 GHz region, and due to the addition of non-magnetic ingredient CNTs, the imaginary part of permeability is lower than that of all of other samples in the test frequency.

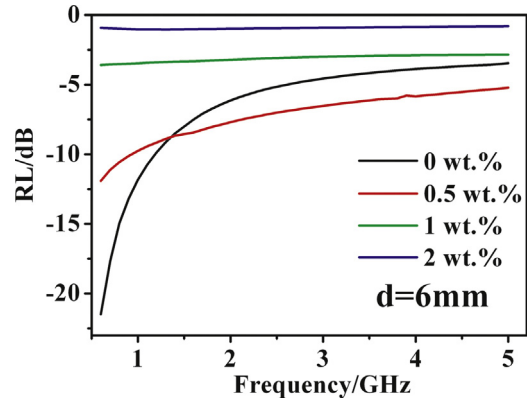


Fig. 9. Frequency dependence of the dielectric loss factor and the magnetic loss factor of CNTs–Ni<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub> composite bulks sintered by microwave at 1000 °C for 1 h with different CNTs content.

According to the measured results of  $\epsilon_r$  and  $\mu_r$  shown in Figs. 7 and 8, the reflectance loss (RL) of CNTs/Ni<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub> composite bulks at 6 mm thickness versus frequency was calculated by the following equations<sup>37</sup>:

$$Z_{in} = \sqrt{\frac{\mu_r}{\epsilon_r}} \tanh \left[ j \frac{2\pi f d}{c} \sqrt{\mu_r \epsilon_r} \right] \quad (1)$$

$$R = 20 \log \left| \frac{Z_{in} - 1}{Z_{in} + 1} \right| \quad (2)$$

where  $\mu_r$  and  $\epsilon_r$  are the complex magnetic permeability and the complex permittivity respectively,  $f$  the frequency,  $d$  the thickness and  $c$  the speed of light.

Fig. 9 shows the relationship between the RL and the frequency in the 0.6–5 GHz range for the samples with different content of CNTs. At the thickness of 6 mm, the RL values of all samples decrease at high frequency. The RL values of CNT-free Ni<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub> composite decreases significantly in the 0.5–2 GHz range, and may appear an absorption peak in the low bands. And for the 0.5 wt% CNT/Ni<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub> composite, RL value becomes higher than that of pure ferrite at high frequency for the enlarged both dielectric loss and magnetic loss (Figs. 7 and 8). Che et al.<sup>38</sup> reported that, compared with pure CNTs and CoFe<sub>2</sub>O<sub>4</sub> nanoparticles, CNTs/CoFe<sub>2</sub>O<sub>4</sub> nanocomposites exhibited improved microwave absorption, and suggested that this improvement might originate from the better match between dielectric loss and magnetic loss. In the present work, this rule is also applicable. It is obvious that in the high CNT content composites, the magnetic loss decreases a lot for the low imaginary permeability (Fig. 8b), but their dielectric loss increases (Fig. 7b). Thus, in order to achieve optimum attenuation effect, the CNTs need to be controlled at lower content than 1 wt%.

#### 4. Conclusion

In summary, CNT/Ni<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub> composites were fabricated by microwave sintering technology. In the microwave processing, CNTs act as susceptors and promoted the consolidation of composites. 2 wt% and 5 wt% content of CNTs in

the composites induced decomposition and reduction of ferrite ceramics for the local ultra-high temperature building up in the interface of CNTs and matrix. Due to the entangled network of conductive pathway formed in the CNT/Ni<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub> composites, the electrical conductivity increased by 7 orders in magnitude in comparison with pure Ni<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub>. Even though the temperature decreased from 300 K to 70 K, the electrical conductivity remained at 0.1 S/m for the 1 wt% CNT/Ni<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub> composites. The CNT/Ni<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub> composites showed an improved microwave attenuation capability at the frequency of 0.6–5 GHz region at 0.5 wt% CNT loading. The present work indicates that CNT/ferrite composites may have potential applications as absorber materials at low temperatures in the advanced particle accelerator of HOM loader.

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