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# Microwave sintering carbon nanotube/$Ni_{0.5}Zn_{0.5}Fe_2O_4$ composites and their electromagnetic performance

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**Abstract**

Carbon nanotube (CNT)–$Ni_{0.5}Zn_{0.5}Fe_2O_4$ 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 $Ni_{0.5}Zn_{0.5}Fe_2O_4$, and remained a high value at the temperature of 70 K (for example, 1 wt% CNT/$Ni_{0.5}Zn_{0.5}Fe_2O_4$ 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 $\varepsilon_r$ and $\mu_r$, the frequency-dependent reflectance loss (RL) of CNT/$Ni_{0.5}Zn_{0.5}Fe_2O_4$ 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.


*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,[1–3] 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.[4–7] 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.[8,9] Since their discovery by Iijima in 1991,[10] 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.[11] When CNTs were incorporated into $NiFe_2O_4$ ferrite, the electrical conductivity of composite increased by 5 orders of magnitude at room temperature after addition of 10 wt% CNTs[12]. 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.[13–16] 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.[17,18] It has been observed that microwave-sintering technique can efficiently reduce the grain growth and enhance the densification rate of ceramics.[19–21] 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.[22]

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/$Ni_{0.5}Zn_{0.5}Fe_2O_4$ 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 $Ni(NO_3)_2$, $Zn(NO_3)_2$ and $Fe(NO_3)_3$ 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 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.

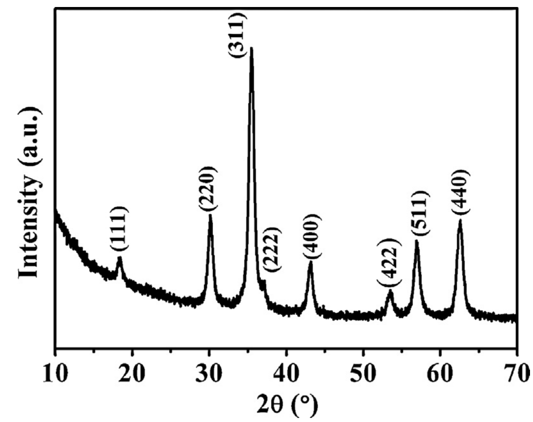


Fig. 1. X-ray diffraction pattern of 2 wt%CNT/$Ni_{0.5}Zn_{0.5}Fe_2O_4$ composites hydrothermally treated at 200 °C for 3 h.

The composite powders were cold pressed into ϕ20*3 $mm^3$ pellets, and then consolidated by microwave sintering (MWS) technology at 1000 °C for 1 h in $N_2$ 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/$Ni_{0.5}Zn_{0.5}Fe_2O_4$ 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.