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Experimental and theoretical investigation of gigahertz nano-metamaterial

Reza Gholipur*, Ali Bahari

Department of Solid State Physics, University of Mazandaran, Babolsar, 4741695447, Iran

HIGHLIGHTS

- $Ag/Zr_{0.9}Ni_{0.1}O_y$ nanocomposites composites were synthesized by co-precipitation technique.
- A negative permittivity and permeability behavior of the M48 and M50 samples was found.
- M50 nanocomposite can realize as a promising candidate for the DNG materials.

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ABSTRACT

Chemical doping of Ag nanoparticles to dielectric medium becomes necessary to create an artificial structure which is useful for various applications, and gives rise to unique properties. Since structurally doped Ag nanoparticles is both of random and ordered, we have prepared $Ag/Zr_{0.9}Ni_{0.1}O_y$ nanocomposites on the random status of this important class of materials. In doing so, effect of Ag content on the structure, electrical, magnetical and optical properties of $Zr_{0.9}Ni_{0.1}O_y$ dielectric was investigated in detail. Characterization of chemically doped Ag also included. It was found that samples with 48 and 50 wt% Ag exhibit the double negative (DNG) properties. That is to say, simultaneous negative permittivity and negative permeability were realized in the $Ag/Zr_{0.9}Ni_{0.1}O_y$ nanocomposites. We believe that the article will be useful to all those interested in DNG metamaterials and provides the present status of the subject.

1. Introduction

Over the last few years, metamaterials have been the area of great interest [1–16], due to their potential applications for superlenses, compact cavity resonators [6,17–19], microwave lens imaging, cloaking [20], and miniaturization of antennas and filters [21]. Metamaterials are engineered materials that obtained their properties from the 2-dimensional or 3-dimensional arrangements of nanostructured particles rather than from fundamental physical properties of their constituents [22–24]. For instance, simultaneous negative permittivity and permeability in such a medium can result in a negative index of refraction [18,23,25,26].

A huge advantage of these artificially structured composites is that, in addition to their chemical composition, they owe their properties to the shape and dimensions of their constituent elements.

By changing the design of unit cell or "meta-atom" the optical properties of the metamaterials can be tailored to reach negative values of effective dielectric permittivity and magnetic permeability thus giving overall negative refractive index in a given frequency range [22–24].

It is imperative now to develop new intuitions and understanding to deal with these materials. Although many developments are only recent, the basic conceptual issues have now been widely debated and reasonably clarified. In general, fabrication metamaterials can be divided into categories: structure of periodic metallic wires and rings [27], inclusions of randomly oriented elongated conducting spheroids [28], and inclusions of systematically oriented elongated conducting spheroids [29]. Fabrication of the periodic metamaterials is usually complicated, which prevent these structures for mass production. To avoid these problems, we have investigated the simple way for synthesizing metamaterials containing randomly much simpler spherical inclusions [30]. Metal-dielectric nanocomposite materials containing

* Corresponding author.
E-mail address: gholipur.reza@gmail.com (R. Gholipur).

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elongated conducting spheroids dispersed in a dielectric matrix have new and unusual properties at high frequency. These nanocomposites have great potential in the preparation of single or double negative materials, as has been shown by Ao et al. [31,32].

In this paper, we are interested in the effective properties of the percolative composites where elongated conducting spheroids are homogeneously distributed. Many percolative composites have attracted much attention as random composites [30].

The elongated conducting spheroids composites are important for industrial applications. Ceramic and plastic materials reinforced by carbon or metallic fibers are becoming increasingly attractive as engineering materials. The physical, chemical and mechanical properties of such materials are the subject of great interest [33,34].

In this paper, we show that Ag metal nanoparticles embedded randomly in $Zr_{0.9}Ni_{0.1}O_y$ dielectric medium (named Mx samples; where "x" is $[Ag]/[Zr_{0.9}Ni_{0.1}O_y] = x$) can exhibit negative permittivity and negative permeability in the microwave wavelength regime.

In the present work, we attribute the negative permittivity to the plasma oscillation of conduction electrons in the Ag nanoparticles, and the negative permittivity behavior is analyzed by Drude model. The permeability of Mx samples, including dielectric with magnetic property and high permittivity can achieve giant response at GHz frequency regime. In general, magnetic response can be obtained via the magnetic resonance excited with eddy currents and magnetic properties of dielectric. Here, we describe the synthesis of Mx nanostructures with *x* values of 0, 5, 48 and 50%. The structural, electrical, optical and magnetical characteristics of Mx were investigated.

2. Experimental

2.1. $Zr_{0.9}Ni_{0.1}O_y$ dielectric synthesis

The solution of $Zr_{0.9}Ni_{0.1}O_y$ dielectric was prepared through co-precipitation technique as follows: First, Zirconyl chloride octahydrate [$ZrOCl_2.8H_2O$] and nickel(II) chloride [$NiCl_2.6H_2O$] were dissolved in deionized water to prepare aqueous solutions with 1 M concentrations, respectively. The molar ratio of the Zr and Ni was Zr:Ni = 9:1. NH_4OH solution was added drop wise to a beaker containing solution with 90 wt% zirconyl chloride octahydrate and 10 wt% nickel (II) chloride stirring by a magnetic stirrer.

2.2. Silver nanoparticles growth

Silver nitrate [AgNO3], n,n-dimethylformamide (DMF) [C_3H_7ON], Polyvinyl pyrrolidone (PVP) and chloroauric acid ($HAuCl_4$) were used as starting compounds. Firstly, $HAuCl_4$ solution was prepared by mixing 10 mL of DMF with 1 mL of 0.005 M $HAuCl_4$. 170 mg of $AgNO_3$ was dissolved in DMF (10 mL) and 170 mg PVP dissolved in DMF (10 mL). A few minutes later, Ag and PVP solutions were added into $HAuCl_4$ solution with the same injection rate of 2 mL/min under vigorous stirring at 1500 rpm at 160 °C for 120 min. Silver nanoparticles began forming at this stage.

The solution was diluted with acetone and centrifuged at 2000 rpm for ~20 min. Ag nanoparticles were dispersed in Zr and Ni solution under vigorous magnetic stirring. The solution was poured into a plastic dish and sonicated for 60 min. The molar ratios of the Ag solution to $Zr_{0.9}Ni_{0.1}O_y$ solution were according to $Ag/Zr_{0.9}Ni_{0.1}O_y = 0$ (named M0), 5 (named M5), 48 (named M48) and 50% (named M50).

2.3. Analyses of phase and morphology

For the crystal and phase analyses, x-ray diffraction (XRD) measurements with Cu Kα (λ = 1.54056 Å) radiation by GBC-MMA007 (2000) were performed. Microscopy analysis and surface morphology were performed using scanning electron microscopy (SEM) and transmission electron microscopy (TEM) techniques. The SEM and TEM images of the films were studied by XL30-PHILIPS and CM10-PHILIPS, respectively.

2.4. The permittivity and permeability measurements

The theories for the permittivity and permeability measurements are "parallel plate capacitor" and "inductance" methods. The parallel plate capacitor method involves sandwiching material between two electrodes to form a capacitor. The inductance method derives the permeability by measuring the inductance of the material. The concept is to wind some wire around material under test and evaluate the inductance with respect to the ends of the wire. The permittivity and permeability as functions of frequency were measured using test fixtures [1] and **HP 8720B** analyzer. The test fixtures consist of material characterized by a permittivity and a permeability denoted by $\varepsilon_e = \varepsilon'_e + i\varepsilon''_e$ and $\mu_e = \mu'_e + i\mu''_e$, respectively.

3. Results and discussion

3.1. Structural and morphological studies of the Mx samples

The XRD patterns of the Mx samples are shown in Fig. 1. Crystalline phases were identified according to the data existing in the ICDD Powder Diffraction File: card no. 00-001-1164 for Ag and card no. 01-081-0610 for $Zr_{0.9}Ni_{0.1}O_y$.

The peaks observed around $2\theta = 38.61°$ in the patterns of Ag doped samples are related to presence of Ag, and the intensity of these peaks increases with increasing of Ag contents. As can be seen from XRD patterns, the peaks related to $Zr_{0.9}Ni_{0.1}O_y$ in the Ag doped samples appeared slightly at bigger 2θ. This observation indicates the of small formation of $Zr_{0.9}Ni_{0.1}O_y$ structure between Ag nanoparticles. The diffraction peaks observed around $2\theta = 38.34$ and 35.11 in M0 and M5 samples, respectively, is attributed to the $Zr_{0.9}Ni_{0.1}O_y$ (042) plane. The absence of this peak in M48 and M50

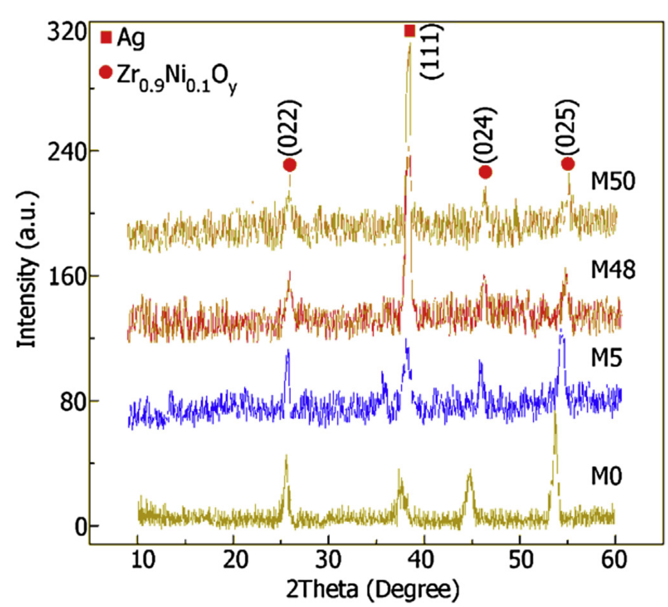

Fig. 1. XRD patterns of the Mx samples.