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A novel microwave absorption material of Ni doped cryptomelane type manganese oxides

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Abstract

Cryptomelane type manganese oxide α-MnO_2 and Ni doped KMn_8O_{16} nanostructures were synthesized by water-bathing methods at 80 °C for 24 h using $NiSO_4 \cdot H_2O$ as the dopant sources. The structures, morphologies and physical properties were investigated by means of X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS). The results show that the products are Ni doped KMn_8O_{16} nanorods after the introduction of $NiSO_4 \cdot H_2O$ during the reaction process. The electromagnetic characteristics and microwave absorption properties of the materials were carried out with a vector network analyzer (VNA) and the transmission line (TML) theory. The dielectric loss and microwave absorption properties of the cryptomelane materials are improved after Ni doping. The thickness dependent reflection loss shows that the peak frequency and effective absorption bandwidth all decrease with the increasing material thickness. With the increase of Ni doping concentration, the peak frequency shifts to higher frequency bands and the effective absorption bandwidth increases. The electromagnetic performance of cryptomelane can be attributed to its unique tunnel structures and the improvement of Ni doping can be due to the enhanced electromagnetic polarization.

Keywords: Cryptomelane manganese oxide; Doping; Dielectric loss; Microwave absorption

1. Introduction

With the increasing requirement and rapid development in electronic industry proliferation of electronic devices such as high-rate data-transferring equipments, portable telecommunication devices and medical equipments, it has resulted in electromagnetic pollution and electromagnetic interference (EMI), which have caused serious environmental disturbances [1]. Thus, electromagnetic wave (EMW) absorbents have gained considerable attention in civil, commercial and military fields because of their shielding and absorption in microwave band range. A good EMW absorbent needs appropriate conductive properties and excellent dielectric or magnetic loss properties to meet the requirements for wider absorption band and higher absorption capability [2]. In the light of this, carbon materials, ferrite composites and metal oxide dielectrics are often chosen as the candidates for their dielectric or magnetic loss properties. To achieve a better performance, morphological tailoring and metal doping are two of the measures that are often taken in practical applications. Nickel is a versatile dopant in materials to improve their dielectric, magnetic and electromagnetic properties. The partial substitution of Ni for Mn in MnZn ferrites can improve their ferromagnetic behavior due to the absence of antiferromagnetic hematice and the less inter- and intra-pores in the doped materials [1]. The influence of Ni doping on multiferroic behaviors in $Bi_4NdTi_3FeO_{15}$ ceramics was found that 10% Ni can increase the space charge created by oxygen vacancies, thus resulting in an improved dielectric loss [3]. Also it is found that Ni doping could improve the magnetic properties of α-MnO_2 to a certain extent [4,5].

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Manganese oxide, constructed of corner- or edge-shared [MnO_6] octahedral units, is one of the largest groups, due to the diversity of their crystallographic structures. Due to their multiple d orbital electrons, quantum size effects and space-confirmed transport phenomena [6], they have used in research, especially in electromagnetic fields [7–9]. Cryptomelane, the 2×2 tunnel structured manganese oxide, including octahedral molecular sieve (OMS) and α-MnO_2, is the most useful and has been most widely studied. OMS with a stoichiometric formula of $KMn_8O_{16} \cdot nH_2O$ (often named as OMS-2) has a pore size of 0.46 nm × 0.46 nm and can accommodate some other metal cations such as Cu^{2+}, Ni^{2+}, Co^{2+}, Fe^{3+} or V^{5+} to stabilize its framework and tune its electrochemical performance, photosensitivity and catalytic activities [10,11]. Besides, potassium ions and water molecules often exist in the tunnels to provide charge balance and structure stabilization [12]. In the review of Suib [6], cryptomelane has mixed valance state of manganese [Mn] and has mobility of lattice oxygen in the cryptomelane surface structure. According to the classical dielectric theory, the polarization of dielectric material in an electromagnetic field mainly resulted from its interface polarization, space charge polarization and relaxation phenomena [13]. The existence of lattice oxygen in the surface of cryptomelane will be beneficial to its dielectric performances. Nevertheless, there are no public reports on the dielectric or electromagnetic properties of Ni doped KMn_8O_{16} materials, to the best of our knowledge.

In the present study, Ni doped KMn_8O_{16} nanostructures were synthesized with facile water-bathing precipitation methods. Their crystalline and morphological structures were characterized and their electromagnetic properties as microwave absorbing materials were also examined.

2. Experimental

2.1. Materials and synthesis methods

All chemical reagents used in the experiments were obtained from commercial sources as guaranteed-grade reagents and used without further purification.

In a typical synthesis, 3 mmol $MnSO_4 \cdot H_2O$ and different ratios of $NiSO_4 \cdot 6H_2O$ were dissolved in 60 ml deionized water separately and magnetically stirred to form homogenous solution. Then the solution was added slowly into a purple $KMnO_4$ solution with 2 mmol $KMnO_4$ pre-dissolved in 40 ml deionized water. After stirring for another 30 min, the dark brown mixture was transferred to a water-bathing with the temperature preset at 80 °C and stayed for 24 h. The solution was cooled down to room temperature naturally. The product was collected by centrifugation and washed with water and absolute alcohol several times. The final powder was dried at 100 °C for 8 h and then collected for characterization. In the synthesis process, the $NiSO_4 \cdot 6H_2O$ was added with the molar ratios of 0%, 5%, 10% and 15% to $MnSO_4 \cdot H_2O$.

2.2. Characterization

The crystallographic structures of the products were investigated using a Japan Rigaku TTR-III diffractometer with Cu kα radiation ($\lambda = 1.5418$ Å) in the range of $2\theta = 10–80°$. The microstructures of the products were observed on a FEI Quanta 200 scanning electron microscopy (SEM) with energy dispersive X-ray (EDX) spectroscopy accessory. X-ray photoelectron spectroscopy (XPS) measurements were performed with a Kratos Amicus X-ray photoelectron specmeter with Alα radiation. The binding energies were corrected by the C 1s peak at 284.6 eV [14].

The electromagnetic properties of the products were characterized by the parameters of complex permittivity and permeability, and were examined on an Agilent N5230A vector network analyzer (VNA) in the 2–18 GHz frequency range. The powders were mixed with molten paraffin wax uniformly with a content of 25 wt% and the mixture was then pressed into toroidal shaped samples with outer diameters of 7.00 mm and inner diameters 3.04 mm. The microwave absorbing properties, in terms of reflection loss (RL), were calculated with the electromagnetic parameters data through the transmission line theory [15,16], as follows:

$$\mathrm{RL} = 20 \log \left| \frac{Z_{in} - Z_0}{Z_{in} + Z_0} \right|,$$
$$Z_{in} = Z_0 \sqrt{\frac{\mu_r}{\varepsilon_r}} \tanh\left(j \frac{2\pi d}{\lambda_0} \sqrt{\mu_r \varepsilon_r} \right) \quad (1)$$

where Z_0 and Z_{in} are the intrinsic impedance of free space and the input impedance of the materials, respectively. λ_0, ε_r, μ_r, and d represent the wavelength of the incident wave in free space, the relative complex permittivity and permeability, and the thickness of the sample, respectively.

3. Results and discussion

3.1. Phase crystallinity

The XRD patterns of the as-synthesized products were shown in Fig. 1. For no Ni doping, the product is a pure tetragonal α-MnO_2 phase (JCPDS 44-0141), without other diffraction peaks of impurities. The peaks of Ni doping products are identified to originate from cryptomelane type manganese oxide (KMn_8O_{16}, JCPDS 06-0547). As presented in Fig. 1, the diffraction peaks become sharper and higher with the molar ratio of $NiSO_4 \cdot 6H_2O$ increasing from 5% to 15%, indicating an improved crystallization of KMn_8O_{16} at a high doping concentration. In addition, the additional peaks of KMn_8O_{16} at (220), (221) and (600) are enhanced. The results indicate that the existence of Ni ions can form KMn_8O_{16} phases and higher concentration of Ni ions can improve its crystallinity, as is shown in Fig. 1(c).

The compositions of manganese oxides were further analyzed by XPS. The high-resolution XPS spectra of pure MnO_2 and 10% Ni doped KMn_8O_{16} are shown in Fig. 2. As shown in Fig. 2(a), the Mn 2p spectrum of undoped MnO_2, the two peaks located at 654.2 and 642.7 eV can be attributed to Mn $2p_{1/2}$ and $2p_{3/2}$, respectively. The positions are very close to the values reported for MnO_2 in the NIST XPS database (653.9 ± 0.2 eV and 641.9 ± 0.2 eV, respectively) and literatures [17,18]. The distance between the two peaks is