



Improved magnetic and microwave absorption properties of manganese nitrides through the addition of ferrous



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ARTICLE INFO

Article history:

Received 24 November 2016

Received in revised form

28 January 2017

Accepted 29 January 2017

Available online 31 January 2017

Keywords:

Manganese nitrides

Complex permittivity

Complex permeability

Microwave absorption

ABSTRACT

(Mn,Fe)-N series micron particles were gotten by high-energy ball milling and consequent annealing of the ferrous and the manganese nitrides powders with different Fe/Mn-N ratios. The phase structures and the magnetic properties, as well as microwave absorption properties of the milled-annealed particles were studied. It was found that phase structures and saturation magnetization M_s changed with the variation of the Fe/Mn-N ratios. The highest M_s about 20.7emu/g was obtained at Fe/Mn-N ratio of 20%. The complex permittivity and permeability behaviors of the milled-annealed particles have been studied in 1–18 GHz. The reflection loss (RL) value exceeding -10 dB at all match thickness and maximum RL values of -23.7 dB with a matching thickness of 2 mm were obtained on particles at Fe/Mn-N ratio of 5%.

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1. Introduction

During the last few years, increasing attention has been focused on microwave absorption materials (MAM) due to the more serious electromagnetic pollution, electromagnetic interference, and urgent military demanding. Magnetic metals and alloys [1,2] ferrite [3,4]s, nonferrite ceramics [5,6] carbon materials [7,8], polymers [9,10] and hybrid materials [11,12] have been studied as MAM. Among the nonferrite ceramics MAM, 3d transition metal nitrides powders such as manganese nitrides [13–15], have attracted more and more attention because they have excellent magnetic, electric, hard, durable, abrasive-resistant, low cost and stable chemical properties [16,17].

It is well known that there are four stable intermediate phases in the Mn-N binary system, including the ϵ phase Mn_4N with fcc structure, ζ phase (Mn_5N_2 , Mn_2N and $Mn_2N_{0.86}$) with a hcp one, and η phase Mn_3N_2 along with θ phase MnN having tetragonal structure. The MnN , Mn_3N_2 and Mn_2N are antiferromagnetic, with Néel temperatures of 650 K, 925 K and 301 K, respectively. The Mn_4N is the only ferrimagnetic phase with a Curie point of 738 K [18]. Thus, the RAM researchers have pay more attention on manganese nitrides particles because the ferrimagnetic properties of Mn_4N phase. Recently, most researchers prepared Mn_4N powders by

nitriding pure Mn powders at high temperatures for a long time [13,14,16,18,19] despite that the nitriding method was time-consuming and energy-wasting. Furthermore, the M_s of these Mn_4N were low at room temperature, which restricts its application. It has been theoretically and experimentally studied that the magnetic and mechanical properties of ferrous nitrides can be improved by Mn-doping [20–22]. Moreover, ferrous atom is next to the manganese atom in periodic table. Furthermore, the structure of Mn_4N and Fe_4N is belong to the same space group. Therefore, the magnetic properties of Mn-N compounds especially the Mn_4N probably can be increased by addition Fe atoms into the Mn-N structures. However, to the best of our knowledge, there are few reports on the influence of doped Fe on the magnetic properties and hence the microwave magnetic properties of Mn-N powders.

In this work, (Mn,Fe)-N micron particles were prepared by high energy ball milling. The as-milled particles were then annealed. The structures, magnetic properties and microwave magnetic properties were investigated.

2. Experimental

Mn-N compounds powders and Fe powders (fabricated by Tianjin chemical industry Co. Ltd.) with different weight percentage ratio (0, 5 wt%, 10 wt%, 15 wt%, 20 wt%, 25 wt%, 30 wt%) of Fe/Mn-N as original materials were mixed in a glove box filled with Argon gas. The mixtures were then high energy ball milled in PM-400 Retsch planetary ball mill with the ball-to-powder ratio of

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10:1 at the rotation speed of 250 rpm for 6 h. Subsequently, the as-milled powders were annealed in vacuum tubular resistance furnace at 873 K for 30min. For convenience, the milled-annealed powders are named sample “0”, “5”, “10”, “15”, “20”, “25” and “30” in accordance with the Fe/Mn-N ratio of 0 wt%, 5 wt%, 10 wt%, 15 wt%, 20 wt%, 25 wt% and 30 wt%, respectively.

The phase constituents of the powders were detected by X-ray diffraction (XRD) with Cu K α radiation. The magnetic properties of the powders were investigated by Vibrating sample magnetometer (VSM). The toroidal composites (the weight ration of the powders/paraffin is about 4:1) were analyzed within the frequency range of 1–18 GHz on a vector network analyzer (Agilent 8722 ES) to extract the complex permeability and permittivity.

3. Results and discussion

The phase structures of the original Mn-N compounds determined by XRD are shown in Fig. 1. We can see that the Mn-N compounds is mainly composed of Mn $_4$ N, Mn $_3$ N $_2$ and Mn $_2$ N $_{0.86}$, along with a trace amount of MnO and Mn.

Fig. 2 is the XRD pattern of milled-annealed powders. Obviously, the average diameter of the grains of the phases in each sample is about several nanometers according to the line broadening degree at half maximum of the diffraction lines. Sample “0” possesses (110), (002), (111), (112), (300), (113) peaks of Mn $_2$ N $_{0.86}$ and (111), (200), (220), (311) peaks of Mn $_4$ N respectively. It also has peaks (111) and (220) which belongs to MnO. From sample “0” to “20”, firstly, it is found that the five samples almost have the same diffraction patterns except that the diffraction intensity of every corresponding peak is different. Secondly, the diffraction peaks are found to shift to high angles from sample “0” to “20”, which means that the lattice parameters are decreasing with the increasing of the Fe/Mn-N ratio. Meanwhile, there are no characteristic diffraction peaks of Fe or Fe-N compounds from sample “5” to “20”, this suggests that the Fe atoms should have solubilized into the matrix of Mn $_4$ N and Mn $_2$ N $_{0.86}$ lattices to substitute for Mn atoms and substitutional solid solutions (Mn,Fe) $_4$ N and (Mn,Fe) $_2$ N $_{0.86}$ have formed which have the same structures as that of Mn $_4$ N and Mn $_2$ N $_{0.86}$. However, the radius of Fe atoms is a little smaller than the Mn atoms, so the lattice sizes of (Mn,Fe) $_4$ N and (Mn,Fe) $_2$ N $_{0.86}$ are smaller than those of Mn $_4$ N and Mn $_2$ N $_{0.86}$. The lattice sizes of (Mn,Fe) $_4$ N and (Mn,Fe) $_2$ N $_{0.86}$ are decreasing as the Fe/Mn-N ratio increases. And therefore, the diffraction peaks shift to higher angles according to Bragg equation. We can see from sample “0” to “20”

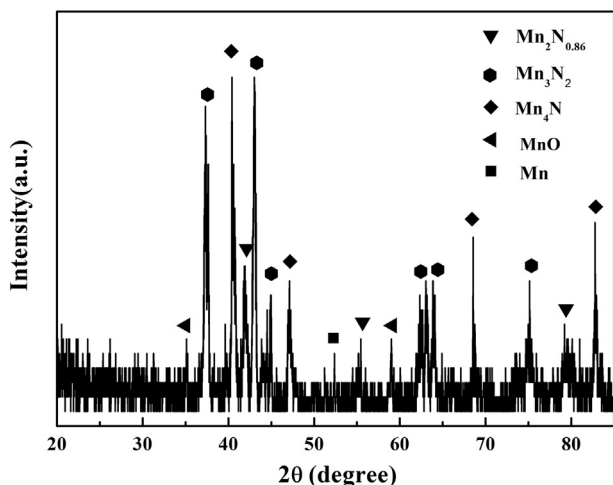


Fig. 1. XRD diffraction pattern of original Mn-N powders.

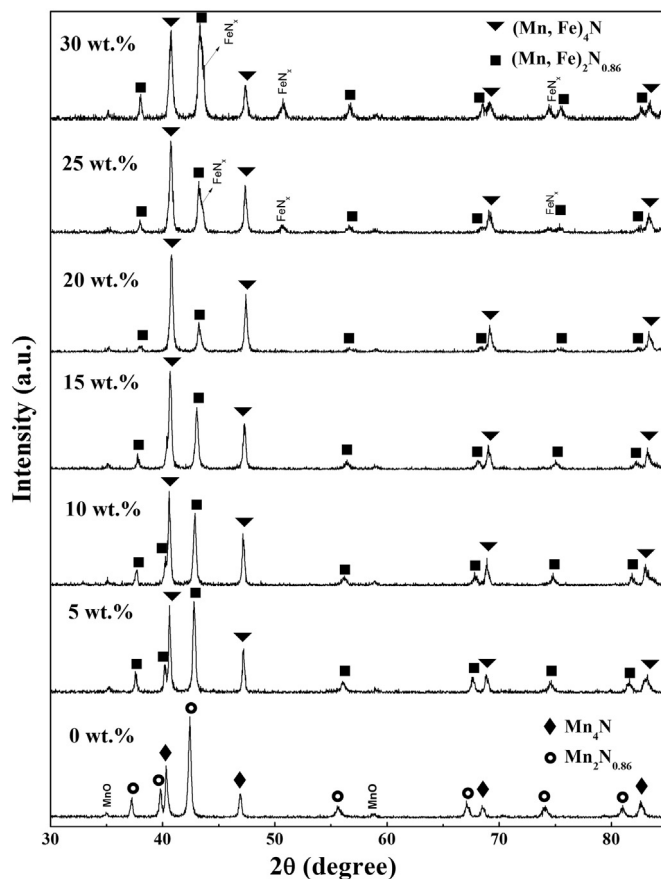


Fig. 2. XRD diffraction patterns of the milled-annealed samples.

that the intensities of Mn $_2$ N $_{0.86}$ peaks gradually decrease as the Fe/Mn-N ratio increases from 0% to 20%. Especially, the (002) peak disappears in sample “20”. Meanwhile, all the intensities of (Mn,Fe) $_4$ N peaks are gradually increasing. From XRD patterns of sample “25” and “30”, we can see that they had almost the same diffraction patterns as sample “20” except that new peaks of FeN $_x$ ($0 < x < 0.05$) at about 42.5, 50.5° and 73.2° appear. The intensities of FeN $_x$ and (Mn,Fe) $_2$ N $_{0.86}$ peaks in sample “30” are stronger than those in sample “25”, while the intensities of (Mn,Fe) $_4$ N peaks are opposite to the former two. These structural revolutions illustrate that the addition of Fe atoms to Mn-N compounds can change the phase structures of Mn-N compounds. Additional, the structural revolution results is similar as the influence results of Mn-doping on the structure of Fe nitrides that the authors has obtained in ref. [21]. The reasons of the Fe contents on the phase revolutions of (Mn,Fe)N are still in investigated.

Fig. 3 shows the M – H loops of the all the samples measured by VSM at room temperature. The saturation magnetization M_s of samples “0” to “30” are about 3.0, 7.1, 10.7, 14.1, 20.7, 15.4 and 8.3 emu/g, respectively. The M_s vs Fe/Mn-N ratio is shown in the inset of Fig. 4. The maximum value M_s of 20.7 emu/g is obtained in sample “20” at the 20 wt%, which is about 30% higher than the M_s of pure Mn $_4$ N powders at room temperature in other literature [13–15,17–19]. Therefore, the addition of proper amount of Ferrous can increase the M_s of manganese nitrides. The enhanced magnetism is highly desirable for device application [22]. The reasons maybe be the following: Firstly, the substitutes of Fe atoms for Mn atoms can lead shorter Fe-Mn or Fe-Fe distances than the former Mn-Mn distances for the sake of smaller Fe atom, and the magnetism of Mn-N compounds are believed to be associated with

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