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Structure and Magnetic Properties of Mn and Al Doped Magnesium Ferrite

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$Mg_{1.3-x}Mn_xAl_yFe_{1.8-y}O_4$ (x=0.1~0.2, y=0.15~0.3) spinel ferrites have been prepared using conventional ceramic technique. Highly densified Mg-Mn-Al ferrites (99% theoretical density) were obtained in this work. The microstructure, magnetic properties and ferromagnetic resonance linewidth (ΔH) of Mg-Mn-Al ferrites have been analyzed by X-ray diffraction, B-H analyzer and FMR spectrometer. The results revealed that all the samples were a single spinel phase. With Mn content increasing and Al content decreasing, both saturation magnetisation ($4\pi M_s$) and Squareness Ratio (SQR) increases, while the coercivity (H_c) first increases and then decreases. In addition, good ferromagnetic resonance linewidth (i.e. ΔH) properties were also realized as 143.8 Oe at 9.3 GHz for the sample with x = 0.17 and y = 0.20. The results imply that $Mg_{1.3-x}Mn_xAl_yFe_{1.8-y}O_4$ ferrites may be applicable for X-band (8~12 GHz) microwave devices.

Keywords: MgMnAl ferrites, Spinel, X-band.

1. INTRODUCTION

A ferrite material is a kind of ceramic compound, which is composed of iron oxide and one or more other metals in chemical combination. Ferrites are commonly used in microwave applications for various non-reciprocal devices such as isolators, circulators, diplexers, filters, phase shifters, etc(1-3). Each kind of microwave device was developed by use of gyromagnetic effect, nonlinear effect and unique electromagnetic characteristics of microwave ferrite under magnetic field and microwave signal(4-5). The properties of microwave ferrite were improved by means of appropriate chemical substitution to achieve different band demands. The requirements for a microwave ferrite are discussed by BaBa et al.(6). In practical application, such materials should have a low dielectric loss, a low magnetic loss at the operating bias field, a low coercive force (H_c), a low ferromagnetic resonance linewidth (ΔH), and a high Squareness Ratio (SQR), i.e., SQR= $B_r/4\pi M_s$. Moreover, a minimal variation in these parameters with variations in temperature is also desirable.

Magnesium-manganese ferrites are widely used in switching devices due to their spontaneous rectangular-hysteresis-loop behavior with a high squareness ratio(7-8). For the application of switching devices such as phased array radar systems, ferrite material with low field loss properties at the frequency of operation is essential for low insertion loss. This indicates that the proper saturation moment must be chosen, and that a relatively narrow linewidth, having a small anisotropy field, is the best choice. Classification of microwave frequency bands are as shown in Table 1. For S-band radar operation, garnet with $4\pi M_s$ values in the range of 600 to 800 gauss are used, whereas X-band radars usually require garnets or spinels of 1400 to 2200 Gauss in the allocated frequency band. Magnesium-manganese ferrite or yttrium-iron garnets, with aluminum or gadolinium substitution for control of saturation magnetization are generally utilized to satisfy these criteria(9-10). In the present work, the effect of substitution of the Mn and Al ions on magnetic properties of the Mg ferrites has been systematically studied. The Mg-Mn-Al composite microwave ferrite with excellent performance was obtained, which is applicable to X-band latching phase shifter devices.

2. EXPERIMENT

The raw materials of Fe_2O_3, MnO_2, $MgCO_3$ and Al_2O_3 with a purity of more than 99 % were adopted. The raw materials should be weighed with an accuracy of 0.0001g according to the chosen stoichiometry of $Mg_{1.3-x}Mn_xAl_yFe_{1.8-y}O_4$. The molecular formulas of four samples were as shown in Table 2. The raw materials were mixed with ZrO_2 balls, water and alcohol according to a certain proportion and then were ground for 2

Table 1 Classification of microwave frequency bands

L band	1 to 2 GHz
S band	2 to 4 GHz
C band	4 to 8 GHz
X band	8 to 12 GHz
Ku band	12 to 18 GHz
K band	18 to 26.5 GHz
Ka band	26.5 to 40 GHz
Q band	33 to 50 GHz
U band	40 to 60 GHz
V band	50 to 75 GHz
W band	75 to 110 GHz

Table 2 The molecular formulas of four samples

Sample	Molecular Formula
A	$Mg_{1.20}Mn_{0.10}Al_{0.30}Fe_{1.50}O_4$
B	$Mg_{1.16}Mn_{0.14}Al_{0.25}Fe_{1.55}O_4$
C	$Mg_{1.13}Mn_{0.17}Al_{0.20}Fe_{1.60}O_4$
D	$Mg_{1.10}Mn_{0.20}Al_{0.15}Fe_{1.65}O_4$

hours by a ball milling machine. Afterwards, the samples were dried and then calcined in the air at 1100 °C for 2 hours with a heating rate of 5 °C /min. After calcination, the powder samples were further ground by a vibration mill for 2 hours. The magnetic powder was processed into cylindrical molds. The cold-isostatic pressing was conducted on the samples to improve uniformity and density of the green bodies. Then, the sample was sintered in oxygen at 1350 °C for 6 hours with a heating rate of 5°C/min. Finally, the sintered bodies were mechanical processed into toroidal cores for measuring the magnetic properties of ferrites according to IEC60556.

The crystalline phase properties were characterized by X-ray Diffractometer (XRD). The magnetic properties ($4\pi M_s$, B_r, H_c, SQR) of the toroidal core was analyzed by Yokogawa SK-130 B-H tracer. A curie temperature measurement was performed by using an Agilent 4294A impedance analyzer with a frequency of 100 kHz. The ferromagnetic resonance linewidth was analyzed by ferromagnetic resonance analyzer.

3. RESULTS AND DISCUSSION

3.1 X-ray diffractom analysis

The structural study is essential for optimizing the properties needed for various applications. The diffraction spectrums were as shown in Fig.1. The XRD pattern of all the samples, showing well-defined reflection without any extra phases, exhibits the formation of a single phase spinel structure. The inter-planar spacing d and Miller indices (hkl) were obtained by XRD analysis. The lattice constant (a) was determined by the Nelson–Riley extrapolation method(11). Results are presented in Table 3 which is found to increase from sample A to sample C then remain the same under the condition of MF-D. From sample A to sample D, the Mg^{2+} and Fe^{3+} in samples were gradually replaced by Mn^{2+} and Al^{3+} ($Mg_{1.3-x}Mn_xAl_yFe_{1.8-y}O_4$，$x$=0.1→0.2，$y$=0.3→0.15). The increase in the lattice constant can be attributed to the ionic size difference as substituted by the large ionic size Mn^{2+} and Fe^{3+} with that of Mg^{2+} and Fe^{3+} ions, respectively (Mn^{2+} : 0.80Å > Mg^{2+} : 0.65Å ; Al^{3+} : 0.50Å < Fe^{3+} : 0.76Å).

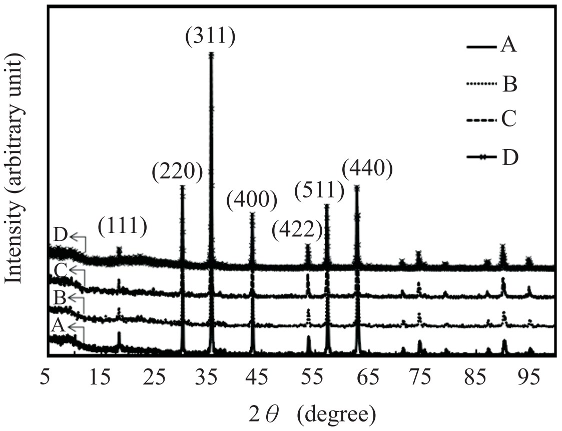

Fig.1. XRD patterns of $Mg_{1.3-x}Mn_xAl_yFe_{1.8-y}O_4$ ferrites with different Mn and Al concentrations.

Simultaneously, the theoretical density ρ_{the} of each sample was calculated according to equation (1), and the experimental values ρ_{real} were measured by Archimedes method. The results are shown in Table 3. It was clearly shown that the density of the sintered ferrite material was as high as 99% theoretical density, which suggests that all samples were well-densified at 1350°C in an oxygen atmosphere.

$$\rho_{the} = Z(MW)/N_A V \; ; \; [g/cm^3] \qquad (1)$$

Z referred to the number of molecules in unit cell.
MW referred to relative molecular mass.
N_A: Avogadro's number = 6.02×10^{23}
V: unit cell volume
MW/N_A: the relative molecular mass of one molecule.

3.2 Magnetic properties

The insertion loss of a microwave device, when the ferrite magnetisation is chosen correctly for the required frequency range, was determined by the dielectric and magnetic loss of the ferrite. Mg-Mn based ferrite usually has low magnetic loss and dielectric loss. The saturation magnetization of these ferrites are around 2000 G and it can be altered by cationic substitution for Fe^{3+} ions.

Two factors influencing the frequencies for which physical realization of the phase shifters is practical are the device geometry and the saturation magnetization of the ferrite used to construct the device. The sum of total losses exhibits a fairly broad minimum value in the range(12).

$$0.2 \leqq (\omega_m/\omega) \leqq 0.6 \quad (2)$$

$$\omega_m = 2\pi\gamma(4\pi M_s)$$

Where γ = 2.8 MHz/Oe is the gyromagnetic ratio of microwave ferrites, and ω is the operating microwave frequency. Above this range, low field magnetic loss generally precludes operation while below this range the device becomes excessively long, resulting in increased loss and weight. In order to meet the operation frequency of 10 GHz (X-band), $4\pi M_s$ of ferrite material should be about 1430 G by calculation. Non-magnetic ions, such as Al^{3+}, Ti^{3+}, and so on, have a strong B-site preference and replace Fe^{3+} in the spinel system(13). Theoretically, the higher the Al^{3+} concentration was, the lower the $4\pi M_s$ was. In this paper, Al^{3+} content was appropriately adjusted to effectively control $4\pi M_s$ so as to be in accord with the application frequency band.

Then B-H Loops of four samples were as shown in Fig.2, and the magnetic properties of samples were as shown in Table 4. It can be clearly seen in Table 4 that with the increase of Mn^{2+} and decrease of Al^{3+}, the $4\pi M_s$ increased. The observed variation can be explained on the basis of difference in magnetic moments of the A and B sub-lattices. In four samples, sample C has a $4\pi M_s$ of approximately 1349 G which was closest to our predetermined target.

The ferrite materials must also have a high squareness value and possess a small coercive force to minimize the control power requirement. As could be seen in Table 4, the squareness increased with the increase of Mn^{2+}. In general, Mn is added in spinel ferrites for two reasons: to diminish the dielectric loss and to reduce the magnetostriction constants(14). As a result, the coercivity and squareness are improved. In this work, the squareness of both sample C and sample D reached more than 0.9. Moreover, the coercivities of these two samples were less than 1.5 Oe, which is good enough for a particular application.

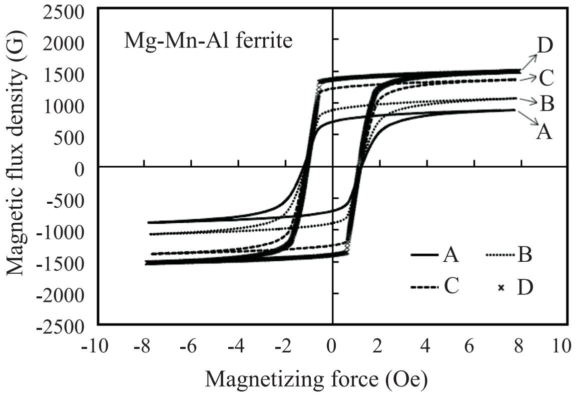

Fig.2. The B-H loops of $Mg_{1.3\text{-}x}Mn_xAl_yFe_{1.8\text{-}y}O_4$ ferrites.

Table 3 Calculated lattice constant, theoretical density and sintered density of $Mg_{1.3\text{-}x}Mn_xAl_yFe_{1.8\text{-}y}O_4$ ferrites

Sample	Lattice constant (Å)	Theoretical density (g/cm^3)	Sintered density (g/cm^3)
A	8.34	4.27	4.24
B	8.35	4.31	4.30
C	8.36	4.38	4.34
D	8.36	4.44	4.38

Table 4 Magnetic properties of $Mg_{1.3\text{-}x}Mn_xAl_yFe_{1.8\text{-}y}O_4$ ferrites

Sample	$4\pi M_s$ (G)	B_r (G)	H_c (Oe)	SQR	ΔH (Oe)
A	958	750	1.55	0.78	214.3
B	1110	951	1.61	0.86	182.8
C	1349	1201	1.48	0.89	143.8
D	1521	1396	1.36	0.92	192.0

The resonance linewidth for nonresonant devices should be as narrow as possible. Excessive linewidth will result in increased insertion loss of a nonresonant device. However, not all microwave devices required minimization of resonance linewidth, for example, the resonant isolator designed by using the ferromagnetic resonance absorption characteristics required the ferromagnetic resonance linewidth to be slightly wider, thus reaching the broadband operation. Therefore, different kinds of microwave devices had different requirements, but ΔH of most of the microwave devices still should be as small as possible. To further characterize the magnetic losses of our samples, the ΔH was measured and as shown in Table 4. Increased ΔH could be caused either by pores and other inclusions in the ferrite or higher anisotropy due to random orientation of grains in the ferrite. For the four samples, ΔH of sample C was the smallest, at about 143.8 Oe.

3.3 Curie temperature measurement

Thermal energy can cause the magnetic dipole moment of ferromagnetic material to deviate from perfect parallel alignment. With the increase of temperature, as the thermal energy was more than the exchange energy of parallel alignment of magnetic dipole moment, the alignment order became messy due to the magnetic moment disturbance by thermal excitation. At this moment, ferromagnetism of ferromagnetic material disappeared, thus transforming into paramagnetism. This temperature as magnetic properties changed was the Curie temperature T_c. When the temperature of ferromagnetic material decreased to less than T_c, the magnetic domain of ferromagnetic material would be formed again, as well as the material obtained the ferromagnetic characteristics again. So the Curie temperature represented the stability characteristics of the material. Whether the devices worked in a resonant magnetic field, above or below resonant field, the loss of power would directly convert into thermal energy, then the temperature of microwave devices would rise. Thus, a higher Curie temperature could ensure that the devices would not be ineffective due to temperature rise as continuous operation.

The thermal variation of initial permeability, μ_i is as shown in Fig.3. T_c of the studied ferrite system has been determined from the μ_i-T curves where a Hopkinson type of effect has been observed. Furthermore, the T_c of samples were listed in Table 5. Obviously, the T_c of four samples regularly increased with decreasing non-magnetic Al content. The linear increase of T_c may be explained by the modification of the A-B exchange interaction strength due to the change of the cation distribution between A and B sites when non-magnetic Al is substituted into the spinel structure. Similar phenomena with a high content of non-magnetic such as Cd and Al is generally observed in Li and Mg based ferrites(15). In addition, the T_c of all samples reached more than 180 °C, which is high enough to meet the application of microwave devices with general power.

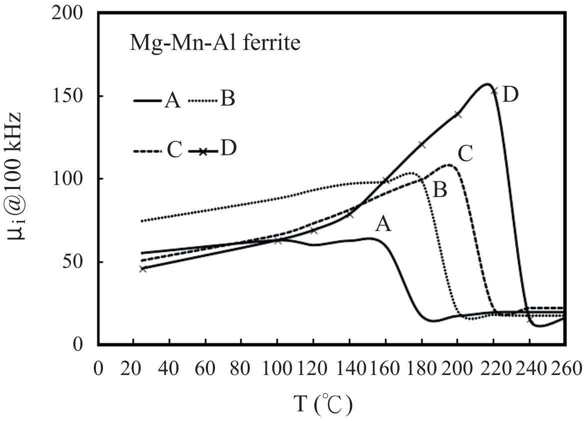

Fig.3. Initial permeability as a function of temperature.

4. CONCLUSIONS

A microwave device may fail to achieve the expected effectiveness if the selected ferrite material was not appropriate. Device properties involve a number of parameters which are interrelated by the intrinsic characteristics of ferrite material. In this work, highly densified Mg-Mn-Al ferrites (99% theoretical density) were obtained and the influence of Mn and Al substitution

Table 5 Initial permeability and Curie temperature of $Mg_{1.3-x}Mn_xAl_yFe_{1.8-y}O_4$ ferrites

Sample	L (μH)	Q	μ_i@100 kHz	T_c (℃)
A	1.75	6.82	56	180
B	2.18	8.29	75	200
C	1.45	4.83	51	220
D	1.45	5.50	46	240

on the characteristics of these ferrites have been studied. The results show that with the decrease of the substitution the amount of Al, the $4\pi M_s$ in samples increases. After adjusting the content of Al, $4\pi M_s$ of sample C tends to 1349 G, which is appropriate for a 10 GHz working frequency. It was also found that with the increase of substitution amount of Mn, Squareness Ratio increases. In $Mg_{1.3\text{-}x}Mn_xAl_yFe_{1.8\text{-}y}O_4$ ferrites, as x was more than 0.17, SQR could reach more than 0.9. Moreover, the ferrite resonance linewidth of sample C was the smallest, and the Curie temperature of sample C could also reach 220 ^{o}C, which can be high enough to meet the application of microwave devices with general power. Hence, through analysis, sample C ($Mg_{1.13}Mn_{0.17}Al_{0.20}Fe_{1.60}O_4$) might be suitable for microwave devices with the working frequency of about 10 GHz.

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