MICROSTRUCTURE, MAGNETIC PROPERTIES AND MICROWAVE ABSORPTION OF $BaFe_{(12-x)}Mn_xO_{19}$ MAGNETIC MATERIALS

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Abstrak - *Dalam penelitian ini telah dibuat magnet lunak berbasis $BaFe_{(12-x)}Mn_xO_{19}$ untuk aplikasi material absorber dengan membuat variasi nilai x = 0 and 1.5 (% mol) menggunakan metode reaksi padat-padat. Bahan baku yang digunakan antara lain barium carbonate ($BaCO_3$), hematite (Fe_2O_3) dan manganese oxide (MnO). Bahan baku yang telah digiling dengan ball mill dikalsinasi pada suhu 1000 °C selama 2 jam dan dicetak pada tekanan 1,3 tonf/cm^2 dengan aditif 3 wt% Celuna WE-518. Sample cetak kemudian disinter pada suhu 1100^{0}C (2 jam). Dari hasil analisis mikrostruktur diketahui bahwa kristal $BaFe_{12}O_{19}$ telah terbentuk dengan parameter kisi sebesar a = b = 5.865Å, dan c = 23.099 Å dengan ukuran partikel < 2 µm. Analisis unsur penyusun material menggunakan µXRF menunjukkan bahwa magnet $BaFe_{10.5}Mn_{1.5}O_{19}$ tersusun atas Fe = 86.577, Ba = 12.433, Mn = 0.331 wt.%. Pengukuran gaussmeter pada magnet $BaFe_{(12-x)}Mn_xO_{19}$ menunjukkan bahwa aditif Mn sedikit menurunkan nilai densitas fluks magnetik. Efek penambahan Mn pada Kurva hysteresis pada struktur $BaFe_{12}O_{19}$ menunjukkan bahwa terjadi penurunan sifat magnetik yang ditandai pada penurunan nilai remanensi dan koersivitas. Namun demikian, nilai maksimum reflection loss (RL) dari gelombang mikro dari $BaFe_{10.5}Mn_{1.5}O_{19}$ dihasilkan sebesar -24.2 dB pada frekuensi 8.98 GHz dengan absorpsi optimum sebesar 99.80% pada frekuensi 4.81GHz. Hal ini menunjukkan bahwa penambahan aditif Mn pada struktur Barium Heksaferit menghasilkan material yang menjanjikan untuk aplikasi penyerap radar (RAM).*

Kata kunci **:** *Magnet Lunak, Barium Hexaferrite, Mangan Oxide, Radar Absorber Materials (RAM)*

Abstract - *$BaFe_{(12-x)}Mn_xO_{19}$ soft magnet for absorber material applications have been produced by the variation of x = 0 and 1.5 (% mol) using a solid state reaction method. The raw materials used are barium carbonate ($BaCO_3$), hematite (Fe_2O_3) and manganese oxide (MnO). The ball milled raw materials were calcined at the temperature of 1000^{0}C for 2 hours and compacted using a pressure of 1.3 tonf/cm^2 with additive of 3 wt% Celuna WE-518. Compacted samples were sintered at the temperature of 1100^{0}C (2 hours). The microstructure analysis showed that the crystal structure of $BaFe_{12}O_{19}$ has been obtained with the lattice parameters of a = b = 5.865Å, and c = 23.099 Å with particle size < 2µm. The element analysis by µXRF on $BaFe_{10.5}Mn_{1.5}O_{19}$ magnet shows that the material was consisted of Fe = 86.577, Ba = 12.433, and Mn = 0.331 (wt%). We observed that the addition of Mn was slightly reduced the magnetic flux density and decreased the magnetic remanence and coercivity. However, the $BaFe_{(12-x)}Mn_xO_{19}$ magnets microwave properties showed that the maximum reflection loss (RL) value on $BaFe_{10.5}Mn_{1.5}O_{19}$ is -24.2 dB at the frequency of 8.98 GHz with optimum absorption is 99.80% at the frequency of 4.81GHz. This experiment showed that the addition of Mn to Barium Hexaferrite structure is promising for application of radar absorbing material (RAM).*

Keywords **:** *Soft Magnet, Barium Hexaferrite, Mangan Oxide, Radar Absorber Materials (RAM)*

I. INTRODUCTION

Ferrite or ceramic magnet usually obtained from the composite powders that consist of ferrite oxide [1]. Magnet can be classified into two types, soft and hard magnet. On soft magnet, the magnetic induction can be disappeared if the external field is released. On the other hand, the magnetic properties of hard magnets are relatively permanent although there is no external magnetic field [2]. Material of anisotropic or isotropic barium hexaferrite magnet are widely used because of its relatively low cost, high energy and can act as an electrical insulator and have a good capability related to demagnetization [3].

Barium ferrite is widely used for many applications, such as in recording media, electrical motor or as electromagnetic wave absorption material. The reason is because of its high saturation magnetization, coercivity, magneto-crystalline anisotropy field and also excellent chemical stability [4]. The combination of the intrinsic behaviour between the magnetic and electrical properties of the ferrite makes it suitable for radio detection and ranging (Radar) applications [5-7].

Several researches made effort to improve its magnetic properties by using substitution of Co-Ti [8], Zn-Ti [9] and Mn [10, 11] to get an optimum condition for an appropriate application. Ghasemi et.al, 2006 analyzed and characterized the electromagnetic properties of barium hexaferrite doped by Mn, Cu and Ti and show that the ferrite powder particle size depends on the chemical composition thus will affect its properties. As a result the material with thickness of 1.8 mm can be used as a microwave absorber at the frequency of 15 GHz because of its high susceptibility and permeability.

There are two different fabrication processes of ferrite magnet: dry and wet process. The isotropic and anisotropic magnet can be made using the dry process, but the wet process can only make the anisotropic magnet [11]. The isotropic ferrite magnet is not magnetically oriented and it has the same magnetization at all directions. It is different compared to the anisotropic ferrite magnet that have only one oriented magnetization direction, depend on the easy axis magnetization structure. The equipment in the dry process can be easily developed compared to the complicated and high precision equipment on wet process [12]. Ferrite magnet can be produced at the temperature between 1000 – 1350^oC [13] from the mixed of ferrite oxide (Fe_2O_3) and barium carbonate ($BaCO_3$) that consist of metallic oxide. Then the metallic oxides were grinded until it reaches micrometer size particle. For several applications, sometimes is also being added by chemical substances, such as manganese oxide (MnO) [3, 13].

In this research, the barium hexaferrite magnet has been produced from the mixed material of ferrite oxide (Fe_2O_3), barium carbonate ($BaCO_3$) and manganese oxide (MnO) as additive material using the process of mixing, grinding, forming, compacting with an magnetic orientation and sintering. The microstructure powder from the calcination process are analyzed using an X-Ray Difractometer (XRD). The magnetic properties, such as flux density and the hysteresis curve (BH curve) are measured using Gaussmeter permagraph. Other measurements such as microstructure and elemental compound are conducted using a Scanning Electron Microscope (SEM) and Micro X-Ray Fluorescene (µXRF). On the other hand the absorption (A) and the Reflection Loss (RL) were analyzed using a Vector Network Analyzer (VNA).

II. EXPERIMENTAL METHOD

The powders of $BaCO_3$, Fe_2O_3 and MnO were used as the raw materials to prepare the barium hexaferrite magnet material ($BaFe_{12-x}Mn_xO_{19}$). All materials were mixed using a mechanical alloying method (wet milling). The mixing process was done using ball mills with aquades media for 20 hours. The powder was dried at the temperature of 100^oC for 24 hours and calcined at the temperature of 1000^oC for 2 hours. The calcined powder then being crushed and meshed using a sieve with 400 mesh size, then the materials were mixed with celuna polymer (WE-518, 3 % wt) and pressed using a pressure of 1.3 tonf/cm^2.

The sintering process was conducted at the temperature of 1100^oC (held for 2 hours). The characterizations testing consist of XRD, SEM and Micro X-Ray Fluorescene (µXRF) analysis, magnetic properties measurements (flux density, B-H curve) and VNA analysis. The flowchart of sample preparation and characterization of $BaFe_{(12-x)}Mn_xO_{19}$ soft magnet is shown in Figure 1.

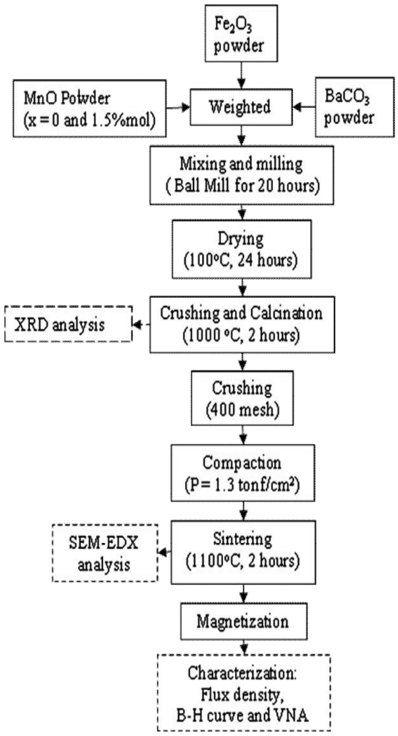

Figure 1. Flowchart of sample preparatian and characterization of $BaFe_{(12-x)}Mn_xO_{19}$ magnet.

III. RESULTS AND DISCUSSION

X-Ray Diffraction (XRD) result of barium hexaferrite ($BaFe_{12}O_{19}$) ceramic magnet material is shown in Figure 2. Based on the phase identification using an XRD, it can be predicted that single phase of barium hexaferrite ($BaFe_{12}O_{19}$) has been obtained by calcined at the temperature of 1000ºC and held for 2 hours. The Rietveld refinement result shows that χ^2 (chi-squared) = $(Rwp/Rexp)^2$ = 0,33. The fitting show a good quality if the R factor is very small. The R factor is a criteria of fit and χ^2 factor is a goodness of fit [14]. The lattice parameters of $BaFe_{12}O_{19}$, respectively are a = b = 5,865 Å, c = 23,099 Å, with the cell volume, V = 794, 25 Å³, and space group P 63/mmc.

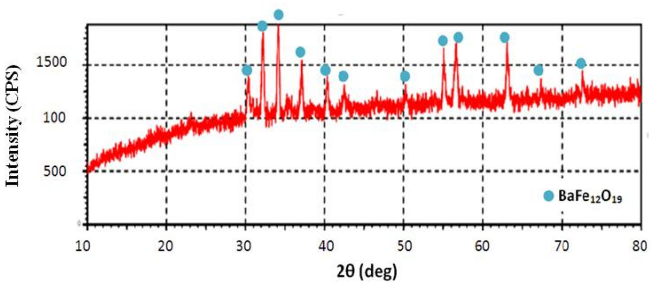

Figure 2. XRD curve of $BaFe_{12}O_{19}$ material after calcination process at the temperature of 1000ºC for 2 hours.

The morphology analysis of $BaFe_{12}O_{19}$ ceramic magnet using a Scanning Electron Microscope (SEM) after the sintering process is shown in Figure 3. The figure also shows that the particle distribution of $BaFe_{12}O_{19}$ magnet is relatively homogeneous with particle size < 2μm.

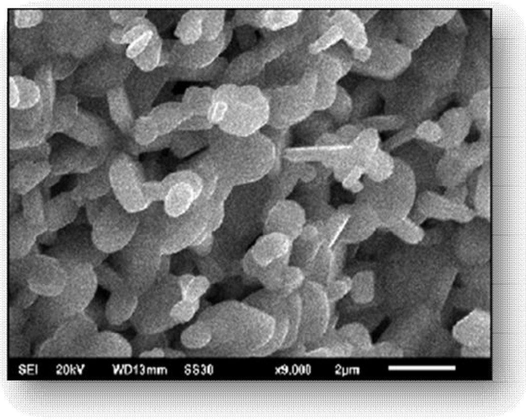

Figure 3. Scanning Electron Micrographs (SEM) analysis of $BaFe_{12}O_{19}$ magnet after sintered at temperature of 1100°C (2 hours).

Figure 4 shows the result of Micro X-Ray Fluorescence (µXRF) analysis, where a). $BaFe_{12}O_{19}$ hard magnet and b). $BaFe_{10.5}Mn_{1.5}O_{19}$ magnet. Based on the analysis using µXRF, it is identified that Ba, Fe, Mn and Zn elements were founded from the used technical material. The amount of elements in $BaFe_{12}O_{19}$ magnet ferrite, respectively are Fe = 87.375, Ba = 11.701, Mn = 0.311 and Zn = 0.608 wt%. On the other hand, the elements found in $BaFe_{10.5}Mn_{1.5}O_{19}$ magnet, respectively are Fe = 86.577, Ba = 12.433, Mn = 0.331 and Zn = 0.658 wt%.

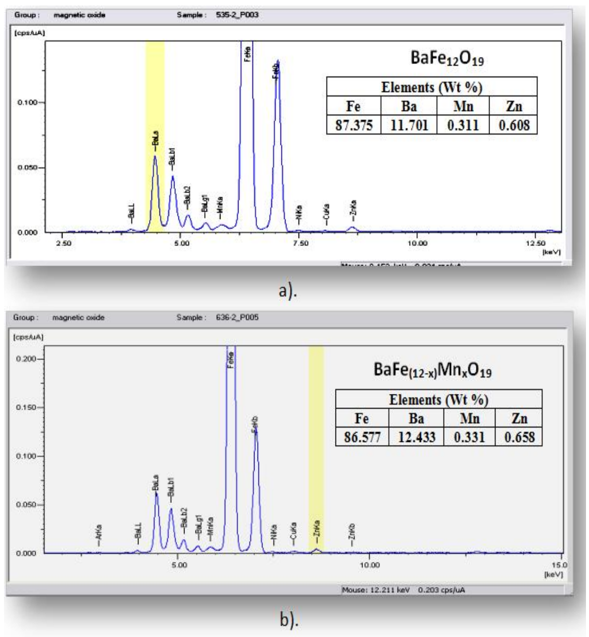

Figure 4. Micro X-Ray Fluorescene (µXRF) analysis, a). $BaFe_{12}O_{19}$ hard magnet and b). $BaFe_{10.5}Mn_{1.5}O_{19}$ magnet

The flux density measurements using a Gaussmeter on $BaFe_{12}O_{19}$ and $BaFe_{10.5}Mn_{1.5}O_{19}$ magnets are shown in Table 1. Based on the measurements, the obtained results were depicted that the optimum sintering condition on both $BaFe_{12}O_{19}$ and $BaFe_{10.5}Mn_{1.5}O_{19}$ magnets were observed at the sintering temperature of 1100°C.

Table 1. Flux density value of $BaFe_{12}O_{19}$ and $BaFe_{10.5}Mn_{1.5}O_{19}$ at sintering temperature of 1000, 1100 and 1200°C.

Materials	**Flux density (Gauss)**		
	Sintered at 1000°C	**Sintered at 1100°C**	**Sintered at 1200°C**
$BaFe_{12}O_{19}$	360.4	404	294
$BaFe_{10.5}Mn_{1.5}O_{19}$	353.8	392	122

B-H curve analysis using a Permagraph is shown in Figure 5. Based on the analysis, it can be concluded that the addition of 1.5% mole of ion Mn could decrease the value of remanence (Br), coercivity (H_{CB}, H_{CJ}) and product energy ($BH_{(max)}$). Therefore it can be used for microwave absorber material. The magnetic properties of ferrite based ($BaFe_{12}O_{19}$ and $BaFe_{10.5}Mn_{1.5}O_{19}$) that have been sintered at the temperature of 1100°C (2 hours) are shown in Table 2.

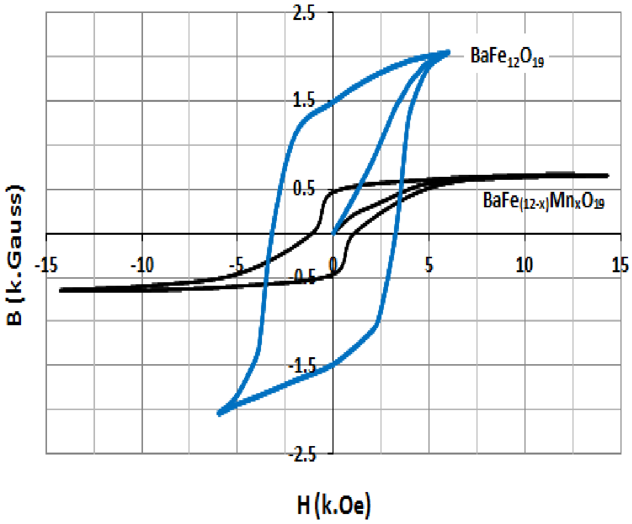

Figure 5. Magnetic hysteresis loops of $BaFe_{12}O_{19}$ and $BaFe_{10.5}Mn_{1.5}O_{19}$ after sintered at the temperature of 1100°C (2 hours).

Table 2. The magnetic properties of ferrite based ($BaFe_{12}O_{19}$ and $BaFe_{10.5}Mn_{1.5}O_{19}$) that have been sintered at the temperature of 1100°C (2 hours).

Material	**Magnetic properties**			
	Br (kG)	H_{CB} (kOe)	H_{CJ} (kOe)	BH_{max} (MGOe)
$BaFe_{12}O_{19}$	1.47	1.28	3.2	0.47
$BaFe_{10.5}Mn_{1.5}O_{19}$	0.49	0.24	1.13	0.12

Theoretically, it is known that $BaO.6Fe_2O_3$ magnet has the value of remanence induction (Br) = 3.2 kGauss, coercivity, H_{CJ} = 3 kOe, and energy product, $BH_{(max)}$ = 2,5 MGOe **[15]**. On the other hand, this research obtains that the magnetic properties of $BaFe_{12}O_{19}$ magnet, respectively are Br = 1.47 kG, H_{CJ} = 3.2 kOe, and $BH_{(max)}$ = 0,47 MGOe. On $BaFe_{10.5}Mn_{1.5}O_{19}$ magnet, the magnetic properties are Br = 0.49 kG, HCJ = 0.24 kOe, and $BH_{(max)}$ = 0.12 MGOe. The difference value between the Mn added and ordinary barium hexaferrite can be caused by the raw material purity, particle size and the making process.

In the correlation of $BaFe_{(12-x)}Mn_xO_{19}$ magnet material application for Radio Detection and Ranging (RADAR), high the reflection loss (RL) and the absorption (A) value of the material are need to be known. Reflection loss (RL) is a parameter to evaluate the microwave absorber that can be defined using the equation below [16]:

$$RL\ (dB) = 20 \log (S_{11}) \tag{1}$$

Absorption value (A) can be calculated using the equation below:

$$A = (1 - S_{11}^2 - S_{21}^2) \times 100\% \tag{2}$$

Where S_{11} and S_{21} are reflection coefficient and electromagnetic wave transmission, respectively. On the other hand the value of reflection loss (RL) and absorption (A), show the capability to absorb the wave within the frequency of 4 – 10 GHz by a Vector Network Analyzer (VNA). Measurement results of Maximum reflection loss (RL) and absorption (A) for ceramic hard magnet are shown in Figure 6 and Table 3. For $BaFe_{12}O_{19}$ ceramic magnet, the value of reflection loss is -15dB at the frequency of 8.92 GHz. On the other hand, the absorption value of $BaFe_{12}O_{19}$ ceramic magnet is 99.86% within the frequency of 8.34GHz.

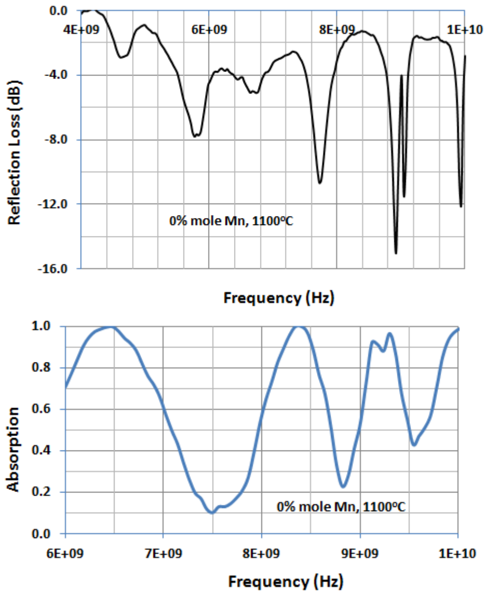

Figure 6. a). Corelation of reflection loss (RL) as a function of frequency and b). Absorption as a function of frequency on $BaFe_{12}O_{19}$ magnet.

Table 3. Absorption of $BaFe_{12}O_{19}$ hard magnet as a function of frequency.

Frequency (GHz)	Absorption (%)	Frequency (GHz)	Absorption (%)
6.48	99.80	9.3	96.50
8.34	99.86	10.00	99.00

For $BaFe_{10.5}Mn_{1.5}O_{19}$ magnet, the relation of reflection loss (RL) and absorption (A) as a function of frequency are shown in Figure 7 and Table 4. The graph shows that the value of reflection loss on $BaFe_{10.5}Mn_{1.5}O_{19}$ ceramic magnet is -24.2 dB within the frequency of 8.98 GHz. On the other hand, the absorption value of $BaFe_{10.5}Mn_{1.5}O_{19}$ magnet is 99.80% within the frequency of 4.81GHz. The results show the reflection loss and absorption is affected by the Mn ion substitution on Fe ion.

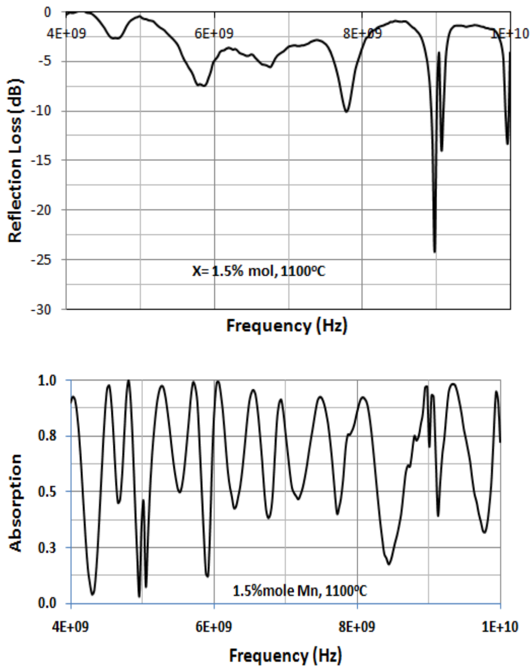

Figure 7. a). Corelation of reflection loss (RL) as a function of frequency and b). Absorption as a function of frequency on $BaFe_{10.5}Mn_{1.5}O_{19}$ magnet.

Table 4. Absorption of $BaFe_{10.5}Mn_{1.5}O_{19}$ soft magnet as function of frequency (4-10 GHz)

Frequency (GHz)	Absorption (%)	Frequency (GHz)	Absorption (%)
4.0	92.6	6.94	91.3
4.54	97.6	7.48	92.5
4.81	99.8	8.08	92.3
5.26	97.2	8.98	97
5.71	99.0	9.34	98.3
6.07	99.1	9.94	94.6
6.55	95.6	-	-

IV. CONCLUSION

$BaFe_{(12-x)}Mn_xO_{19}$ soft magnet for absorber material have been produced by the variation of 0 and 1.5 mole% ion of Mn by using a solid state reaction method. The raw materials are barium carbonate ($BaCO_3$), hematite (Fe_2O_3) and manganese oxide (MnO). The crystal structure of $BaFe_{12}O_{19}$ single phase (calcinated at the temperature of 1000ºC) has the lattice parameters, respectively are a = b = 5.865Å, c = 23.099 Å and V = 794.25 Å^3. The magnet morphology of $BaFe_{(12-x)}Mn_xO_{19}$ that have been sintered at the temperature of 1100ºC and held for 2 hours produce homogenous particles with the size of < 2 µm. The elements on $BaFe_{10.5}Mn_{1.5}O_{19}$ magnet are Fe = 86 - 87, Ba = 11.7 – 12.5, and Mn = 0.31 – 0.33 wt%. The addition of 1.5% mole of Mn ions decreases the flux density value from 404 to 392 Gauss. The addition of 1.5 mole of Mn ions also causes the value of Br, H_{CJ} dan $BH_{(max)}$ decrease, respectively from 1.47 kGauss to 0.49 kGauss, from 3.2 kOe to 1.13 kOe and from 0.47 MGOe to 0.12 MGOe. The optimum reflection loss (RL) and absorption (A) on $BaFe_{12}O_{19}$ magnet were achieved, RL = -15 dB in the frequency of 8.92 GHz and A = 99.86% at the frequency of 8.34 GHz. On the other hand on $BaFe_{10.5}Mn_{1.5}O_{19}$ magnet, RL = -24.2 dB (frequency of 8.98 GHz) and A = 99.80% (frequency of 4.81GHz). This experiment showed that the addition of Mn to Barium Hexaferrite structure is promising for application of radar absorbing material (RAM).

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