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Effect of double-soak sintering on magnetic properties of $Mg_xMn_yAl_zFe_{3-(x+y+z)}O_4$ ferrites

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A study was made to determine the effects of a double-soak sintering process on the saturation magnetization, Curie temperature and hysteresis properties of an Al-substituted MgMn-microwave ferrite. This process decreases saturation magnetization and magnetic induction, while increasing the loop squareness and the Curie temperature. The double-soak sintering process improves the properties of the ferrite for application in a low-microwave-frequency band (i.e. S-band) latching phase shifter. This improvement could not be achieved by increasing the Al^{3+} content, as this tends to reduce the Curie temperature, and thus decreases the thermal stability. The double-soak sintering process, however, enables a composition to be used which initially has a slightly higher saturation magnetization than the desired value.

1. Introduction

The ferrimagnetic materials presently used in digital or latching phase shifters have an unusually large number of constraints applied to them; in addition to the proper control of microwave properties, the characteristics of the hysteresis loop and the Curie temperature, T_c, are also critical [1]. Al-substituted YIG and/or Al-substituted MgMn-ferrite have a narrow linewidth with a low coercive force, H_c, at low saturation magnetization, $4\pi M_s$, and are being widely employed for the latching phase shifter at low microwave frequencies. They have low magnetic and dielectric losses over a wide range of saturation magnetization [1-3]. However, the MgMnAl-ferrites cost approximately one-half the price of YGdAl-garnets and are thus more economical to use. The temperature stability of the former, however, is inferior to that of the garnet due to its low Curie temperature. The temperature dependence of the saturation magnetization, as well as the magnetic remanence, Br, has a strong influence on device performance if variable ambient temperature, or RF power dissipation in the device, produces temperature variation in the ferrimagnets. The temperature stability of the materials usually increases with T_c and is characterized by the slope of M_s versus T, or B_r versus T, curve. It is thus desirable to promote the temperature stability of the ferrite, by increasing T_c while maintaining low $4\pi M_s$, by some means in order to take full advantage of its low cost. An effort to reduce $4\pi M_s$ by chemical means, i.e. by increasing the Al^{3+} content, results in a *reduction* of T_c [4, 5], and this is thus not the most appropriate approach. The problem may, however, be surmounted by a proper physical processing of the material. This paper deals with the property modification of a low cost MgMnAl-ferrite through *the double-soak sintering process*.

The double-soak sintering process consists of a primary high temperature (T_1) sintering followed by a secondary low temperature (T_2) soaking stage. The secondary stage was introduced in order to obtain a low temperature equilibrium state of ionic distribution as a means of property improvement. The process is simple and eliminates the troublesome double "quench" and "temper" operations [3, 6, 7].

The idea of the double-soak sintering process is based upon the changes in cation distribution and oxidation states, of multivalent metallic ions in the spinel lattice, as a function of temperature

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[8-14]. By using the principle and process mentioned above, T_c can be increased while reducing $4\pi M_s$. This is the desired property modification of the MgMnAl-ferrite which is of interest in order to obtain a suitable ferrite for a low-microwave-frequency (i.e. S-band) latching phase shifter.

2. Experimental procedure

The compound $Mg_xMn_yAl_zFe_{3-(x+y+z)}O_4$ with $x = 0.979$, $y = 0.089$ and $z = 0.509$ was prepared from high-purity Baker's $MgCO_3$, $MnCO_3$ and Fe_2O_3, and electronic grade Linde Al_2O_3 by standard ceramic techniques. The powders, in proper proportion, were intimately mixed by ball milling in isopropyl alcohol. The mixtures were calcined at 950°C for 2 h, and then milled for 24 h in alcohol.

3% by weight of paraffin dissolved in warm 1.1.1. trichloroethane was then added to the prepared powders as a binder and lubricant. Rectangular toroids were isostatically pressed at 20 000 psi*. The pressed toroids were then both single- and double-soak sintered in air according to the sintering schedule presented in Table I. The heating rate was maintained at 50°C h^{-1} up to 300°C at which the binder was dried out for 5 h. Up to the primary sintering stage, the heating rate was kept at 100°C h^{-1}. The same cooling rate from the primary sintering stage was maintained down to 1000°C. Below this the cooling rate slowed down and followed the cooling characteristic of the furnace.

TABLE I Sintering schedule. The primed sample codes represent the double-soak sintering.

	First soak		Second soak	
	T_1	t_1	T_2	t_2
Sample	(°C)	(h)	(°C)	(h)
A	1330	24		
A′	1330	24	640	20
B	1400	24		
B′	1400	24	640	20
C	1435	24		
C′	1435	24	640	20

The secondary soaking temperature was kept at 640°C for 20 h to maintain the equilibrium condition of the ferrites.

B–H loop properties were measured by means of an oscilloscope loop tracer at 800 cycles with an applied field $H_a = 5H_c$. $4\pi M_s$ and T_c were measured by a vibrating sample magnetometer at $H_a = 6000$ Oe.

3. Results and discussion

The experimental results are presented in Table II and in Figs. 1 to 3. The values given are the averages of four samples in each lot. The density of the ferrites (Fig. 1) implies that the appropriate firing temperature for these ferrites lies above 1400°C and extends up to 1435°C, which is in agreement with a previous result for MgMnAlFe-ferrite of approximately the same composition [2].

Average grain sizes of the ferrites sintered at 1330°C ranged from 7 to 12 μm. Microstructures of the ferrites sintered at 1400 and 1435°C, however, showed discontinuous grain growth; the former had about 40% of the grains ranging from 40 to 155 μm, while the latter revealed about 55% of the grains ranging from 50 to 400 μm.

As shown in Figs. 2 and 3, above 1400°C, at which an appropriate densification as well as reaction was achieved, $4\pi M_s$ decreases and T_c increases through the double-soak sintering as expected. B_r and B_m decreased with $4\pi M_s$. However, the squareness, B_r/B_m, was found to be improved since the rates of reduction of B_r and B_m were different. The double soaking effect on the ferrites sintered at an initial temperature of 1435°C is noticeably larger. The

TABLE II Magnetic properties of singly and doubly sintered ferrites

Sample	Shrinkage (%)	Density (g cm^{-3})	$4\pi M_s$ (G)	B_m (G)	B_r (G)	B_r/B_m	H_c (Oe)	T_c (°C)
A	17.30	4.1099	1010	833	641	0.77	0.99	150
A′		4.1410	956	905	632	0.70	0.91	139
B	17.93	4.2350	926	768	640	0.84	0.68	148
B′		4.2179	915	765	634	0.83	0.71	154
C	17.49	4.2375	938	848	713	0.85	0.38	138
C′		4.2310	865	697	615	0.88	0.52	155

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*10^3 psi = 6·89 N m^{-2}

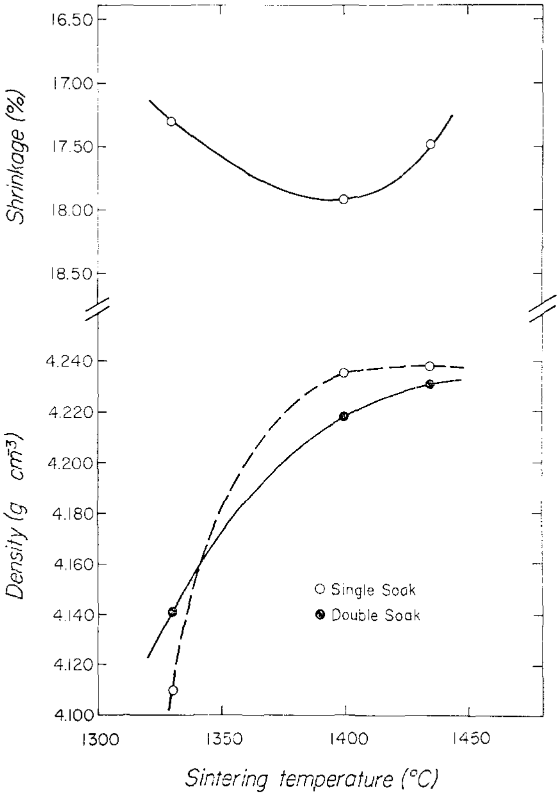

Figure 1 Linear shrinkages and densities versus sintering temperature.

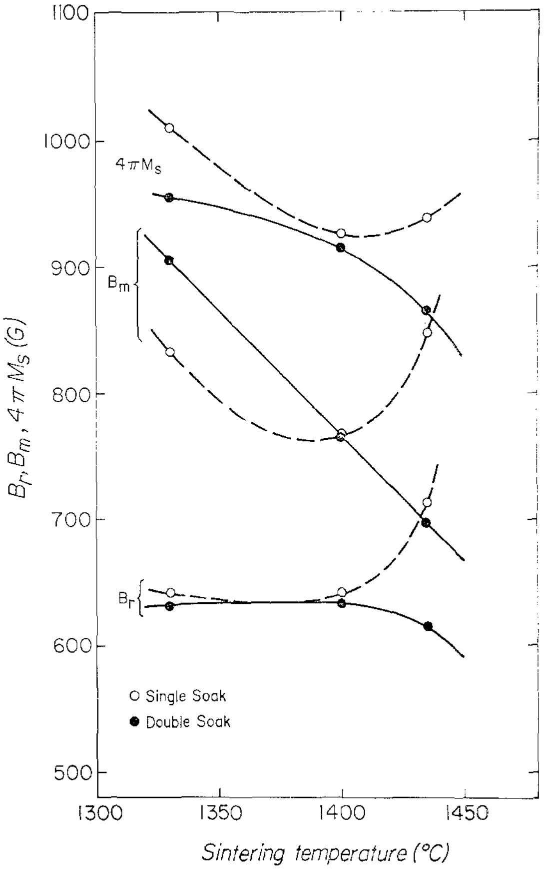

Figure 2 $4\pi M_s$, B_m and B_r versus sintering temperature of single- and double-soaked ferrites.

changes of the above, due to the secondary soaking, yield an improvement in the properties of the ferrites for the low-frequency-microwave phase shifter. H_c is also increased as shown in Fig. 3. Although excessive increases in H_c are detrimental for microwave ferrites, the increased H_c is still low enough for device purposes.

The effects of double-soak sintering on the property variations are attributed to changes in cation distribution between the A (tetrahedral) and B (octahedral) sites, and in the oxidation states of the contributing multivalent cations (in the spinel lattice). The saturation magnetization, Curie temperature, and the cation distribution of ferrimagnetic spinel, can be changed not only by solid solution but also by thermal treatment. Cations with noble-gas configurations: Li^+, Mg^{2+}, Al^{3+}, Ti^{4+}, and those with a half-filled 3d orbit: Mn^{2+} and Fe^{3+}, may occur in both sites in the spinel structure. These ions statistically distribute themselves depending on the temperature and follow a Boltzmann distribution law [8]. The statistical distribution of the ions changes the net magnetic moment of the ferrite as well as the related properties.

Theoretical treatment of site preferences for cations in the spinel lattice has shown qualitative agreement with experiment for simple ferrites [15, 16]. A number of studies for the more complex spinels such as MgMn-ferrites suggested only limited generalizations about valence states and site locations [7, 13, 17, 18]. A generalization of the conclusions of these studies is that magnesium has a preference for octahedral sites; manganese can occupy either site, but has a slight preference for tetrahedral sites; Mn in the Mn^{3+} state, however, prefers to occupy octahedral sites together with Fe^{2+} forming the stable ion pair $[Mn^{3+}Fe^{2+}]$ and iron in the ferrous state usually prefers octahedral sites.

A determination of valence states and site locations of the ions in a MgMn-ferrite is not feasible, because both Fe and Mn can exist in the spinel lattice in two, or even three different

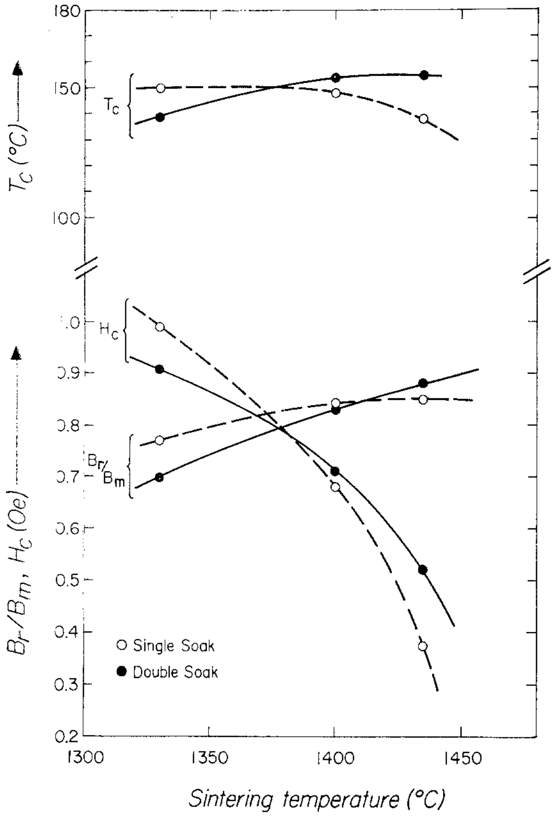

Figure 3 T_c, $\boldsymbol{H}_c$ and $\boldsymbol{B}_r/\boldsymbol{B}_m$ versus sintering temperature of single and double-soaked ferrites.

valence states. The present MgMnAl-ferrite is even more complex than those mentioned above and it may thus exhibit a more complicated physical behaviour, making interpretation of the results rather speculative. Nevertheless, by employing the above-mentioned generalization, an attempt may be made at interpreting the present experimental results in terms of cation distribution, and valence states of some of the ions, as a function of thermal process history.

The chemical formula of the MgMnAl-ferrite can be expressed by $Mg_xMn_yAl_zFe_{1.932-z}O_4$ with $x + y = 1.068$, but to simplify the following discussion the formula will be approximated by $Mg_xMn_yAl_zFe_{2-z}O_4$.

Depending on the ionic states of Mn atoms in the ferrite, two different expressions for the ionic distributions and the related values of saturation magnetic moments, μ_0, are possible:
Case 1: Mn ions exist as divalent (Mn^{2+}) states in both A and B sites. The ionic distribution of Mg, Mn and Al on the A and B sites with their respective distribution parameters, α, β, and γ can be expressed by:

$$\begin{aligned}&[Mg^{2+}_{\alpha x}\,Mn^{2+}_{\beta y}\,Al^{3+}_{\gamma z}\,Fe^{3+}_{1-(\alpha x+\beta y+\gamma z)}]\\ &\qquad\{Mg^{2+}_{(1-\alpha)x}\,Mn^{2+}_{(1-\beta)y}\,Al^{3+}_{(1-\gamma)z}\\ &\qquad\qquad Fe^{3+}_{[(1-z)+(\alpha x+\beta y+\gamma z)]}\,O^{2-}_4\}\end{aligned} \tag{1}$$

where the distribution parameters, α, β, and γ, are respectively fractions of Mg^{2+}, Mn^{2+} and Al^{3+}, ions on the A (tetrahedral) sites.

The saturation magnetic moment in this case is thus

$$\begin{aligned}&\mu_0 = \mu_B - \mu_A =\\ &\{\mu_{Mg}(1-\alpha)x + \mu_{Mn}(1-\beta)y + \mu_{Al}(1-\gamma)z\\ &+ \mu_{Fe}[(1-z) + (\alpha x + \beta y + \gamma z)]\}\\ &- \{\mu_{Mg}\alpha x + \mu_{Mn}\beta y + \mu_{Al}\gamma z\\ &\qquad + \mu_{Fe}[1 - (\alpha x + \beta y + \gamma z)]\}\,.\end{aligned} \tag{2}$$

Since $\mu_{Mg^{2+}} = 0$ Bohr magnetons; $\mu_{Mn^{2+}} = 5$ Bohr magnetons; $\mu_{Al^{3+}} = 0$ Bohr magnetons; $\mu_{Fe^{3+}} = 5$ Bohr magnetons, then

$$\mu_0 = 5[2\alpha x + y + (2\gamma - 1)z]\,. \tag{3}$$

Thus, as the tempering temperature (the secondary soaking temperature in this work) decreases, the number of tetrahedral distribution parameters should decrease and the magnetic moment of saturation magnetization (or maximum flux density) must decrease. Note that Mn^{2+} does not have an effect on the magnetic moment in this case.

Case 2: Mn^{2+} and Mn^{3+} co-exist in the ferrite and, while the divalent ions prefer to sit on tetrahedral sites, the Mn^{3+} reduces some fraction (f) of the octahedral Fe^{3+} to Fe^{2+}. The ionic distribution in this case will be:

$$\begin{aligned}&[Mg^{2+}_{\alpha x}\,Mn^{2+}_{\beta y}\,Al^{3+}_{\gamma z}\,Fe^{3+}_{1-(\alpha x+\beta y+\gamma z)}]\\ &\{Mg^{2+}_{(1-\alpha)x}\,Mn^{3+}_{(1-\beta)y}\,Fe^{2+}_{f(1-\beta)y}\,Al^{3+}_{(1-\gamma)z}\\ &\qquad Fe^{3+}_{[(1-z)+(\alpha x+\beta y+\gamma z)-f(1-\beta)y]}\}O^{2-}_4\,.\end{aligned} \tag{4}$$

The saturated net magnetic moment is then

$$\begin{aligned}&\mu_0 = \mu_B - \mu_A\\ &= \{\mu_{Mg}(1-\alpha)x + \mu_{Mn^{3+}}(1-\beta)y\\ &+ \mu_{Fe^{2+}}f(1-\beta)y + \mu_{Al}(1-\gamma)z\\ &+ \mu_{Fe^{3+}}[(1-z) + (\alpha x + \beta y + \gamma z)\\ &- f(1-\beta)y]\}\\ &- \{\mu_{Mg}\alpha x + \mu_{Mn^{2+}}\beta y + \mu_{Fe^{3+}}\\ &\qquad [1 - (\alpha x + \beta y + \gamma z)]\}\,.\end{aligned} \tag{5}$$

Since $\mu_{Mn^{3+}} = 4$ Bohr magnetons and $\mu_{Fe^{2+}} = 4$ Bohr magnetons

$$\begin{aligned}\mu_0 = {}&10\alpha x +\\ &[4 + (1+f)\beta - f]y + 5(2\gamma - 1)z\,.\end{aligned} \tag{6}$$

The magnetic moment will decrease with the distribution parameters, α, β and γ as the tempering (secondary soaking) temperature decreases. All the cations, Mg, Mn and Al, have an effect on the values of the magnetic moment in this case.

According to the above discussion, regardless of the definite status of the ionic state of the Mn atoms, the saturation magnetization, or maximum flux density, should be reduced, without changing the composition, simply by introducing a secondary soaking stage at a lower temperature than that of the primary sintering temperature. At the same time it is predictable that the Curie temperature of the doubly sintered ferrites is higher than that of the conventionally sintered ferrites, since the number of magnetic ions participating in the A–B interaction increases. As shown in Figs. 2 and 3, above 1400°C, at which an appropriate densification was achieved, the double-soak sintered ferrites reduced $4\pi \boldsymbol{M}_{\mathrm{S}}$ and increased T_{C}, as would be expected from the argument above.

One may speculate that the decrease of the saturation magnetization in the double-soaked samples ($4\pi \boldsymbol{M}_{\mathrm{S}}{}^{\mathrm{D}}$) may be due to the decrease in the density of the samples (d^{D}), since $\boldsymbol{M}_{\mathrm{S}}$, μ_0 and the density, d, are related by $\boldsymbol{M}_{\mathrm{S}} = \mu_0 d$. If this is the case, the percentages of the changes in both, $(d^{\mathrm{D}} - d^{\mathrm{S}})/d^{\mathrm{S}}$ and $(\boldsymbol{M}_{\mathrm{S}}{}^{\mathrm{D}} - \boldsymbol{M}_{\mathrm{S}}{}^{\mathrm{S}})/\boldsymbol{M}_{\mathrm{S}}{}^{\mathrm{S}}$, should be parallel and nearly the same*. The percentage changes are plotted in Fig. 4. This Figure reveals that the percentage decreases in the saturation magnetization for the double-soaked ferrites are much bigger than those of the densities. The decrease in $4\pi \boldsymbol{M}_{\mathrm{S}}$ should thus be attributed to the ionic distribution (at least for the ferrites originally sintered at above 1400°C, at which the original ferrites are fully densified which are the subject of this discussion).

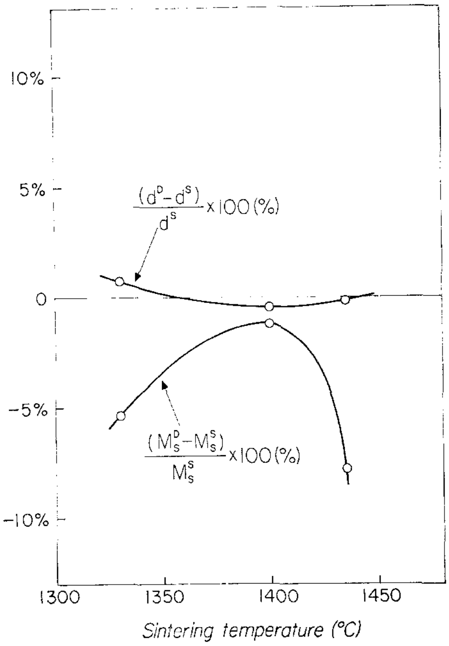

Figure 4 Percentage changes in density and saturation magnetization after double-soak sintering.

The increase in $\boldsymbol{H}_{\mathrm{C}}$ by double-soak sintering may be explained in several ways. The grain sizes for a given composition might be expected to exert a strong influence on $\boldsymbol{H}_{\mathrm{C}}$. The grain sizes of single and double soak sintered samples at temperature above 1400°C showed little difference: the grain size effect on $\boldsymbol{H}_{\mathrm{C}}$ would appear, therefore, not to be an influential factor. $\boldsymbol{H}_{\mathrm{C}}$ has been shown to be less influenced by the porosity of the ferrites than by the grain size [19]. The samples sintered above 1400°C, however, show that $\boldsymbol{H}_{\mathrm{C}}$ varies as $\boldsymbol{M}_{\mathrm{S}}{}^{-1}$. There are a number of different theories for $\boldsymbol{H}_{\mathrm{C}}$ which lead to an inverse dependence on $\boldsymbol{M}_{\mathrm{S}}$. According to Néel [20], for a model in which the $\boldsymbol{H}_{\mathrm{C}}$ is attributed to fluctuations in internal stress, $\boldsymbol{H}_{\mathrm{C}}$ is given by:

$$\boldsymbol{H}_{\mathrm{C}} \sim \frac{(\lambda\sigma)^2}{K\boldsymbol{M}_{\mathrm{S}}} \tag{7}$$

while if $\boldsymbol{H}_{\mathrm{C}}$ is attributed to nonmagnetic inclusions, $\boldsymbol{H}_{\mathrm{C}}$ is given by:

$$\boldsymbol{H}_{\mathrm{C}} \sim \frac{K}{\boldsymbol{M}_{\mathrm{S}}} \tag{8}$$

where σ is the internal stress, λ is the magnetostriction coefficient, and K is the anisotropy constant. Although it is not known what the controlling mechanism for $\boldsymbol{H}_{\mathrm{C}}$ is in the materials, the anisotropy constant, at least, is not greatly affected by the double-soak sintering process in accord with Rado *et al.* [21] who studied the anisotropy of $MgFe_2O_4$ single crystals. Their results showed that the anisotropy was dependent on the Fe^{3+} ion distribution between A and B sites; the change, however, was only 10%. If it is assumed that the term $(\lambda\sigma)$ is relatively constant for the cation distribution in the material, it can thus be stated that whatever the mechanism, the

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*The superscripts, D and S, signify the double and single sintering processes.

parameters involved, λ, σ and K may be relatively constant for the range of cation distribution in this work. Equations 7 and 8 then reduce to:

$$H_c \propto \frac{1}{M_s} \tag{9}$$

4. Conclusion

The experimental results and the discussions may be summarized as follows: the difficulty involved in "property adjustment" of low cost MgMnAl-ferrite suitable for a low-microwave-frequency band latching phase shifter, by substituting non-magnetic Al^{3+} ions can be improved by proper physical processing. By applying the simple double-soak sintering process to MgMn Al-ferrite with a slightly higher value of $4\pi M_s$ than that required, the thermal stability of the ferrite can be improved. The same principle may be extended to ferrites for use in a wide range of lower frequency devices, if one choses an appropriate initial composition of the ferrite and treats it through double-soak sintering. This method, in principle, may also be applied to any "statistical"-type ferrimagnetic material, to achieve similar property modifications.

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