High Resistivity High Initial Permeability Mn-Zn Ferrite Applied for 10 MHz Range

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Abstract:

 JFE Group has successfully developed MnZn ferrite with maintaining high permeability μ$_i$ up to 10 MHz range. The non-conventional choice of the composition, which uses less amount of Fe than the stoichiometric ratio, enabled it to keep its μ$_i$ up to 10 MHz range by suppressing eddy current loss realized by higher resistivity and lower permittivity above 300 kHz. Furthermore, JFE Group has succeeded in preventing magnetic deterioration by substituting part of major component with CoO which can compensate positive and negative magnetocrystalline anisotropy constant K$_1$ to 0, near room temperature. The new material "MR04" has higher μ$_i$, better high frequency characteristics of μ$_i$, higher Curie temperature and magnetic flux density. It is a promising soft magnetic material for magnetic cores of noise filters for automobile applications.

1. Introduction

In recent years, SiC, GaN and other compounds that enable high output, high frequency operation have progressively replaced the conventional Si in power semiconductors used in switching power sources, and the drive frequency of electronic components has increased steadily. Accompanying this trend, high frequency noise occurs, heightening the demand for filters that are capable of removing high frequency noise. In this type of noise filter, a metal powder core or a ferrite core is used as the magnetic core. One property required in magnetic core materials for this application is high initial permeability, μ$_i$, over a wide frequency range.

JFE Ferrite Corporation, a member of the JFE Chemical Corporation Group, has commercialized various high permeability Mn-Zn ferrite products[1].

Among the conventional high permeability materials, MA055 can maintain μ$_i$ up to the highest frequency range, but the μ$_i$ of MA055 also attenuates rapidly in the frequency range exceeding 1 MHz. Therefore, a Mn-Zn ferrite material that can maintain high μ$_i$ up to 10 MHz has long been desired.

Here, when the composition of Mn-Zn ferrite is expressed by the chemical formula $Mn_aZn_bFe_{2+c}O_{4+d}$ (a+b+c=1). In the stoichiometric composition, c=0, that is, the component number of Fe is 2. However, in all the Mn-Zn ferrite products commercialized in the past, c had a positive value, i.e., the component number of Fe was 2 or more. In this paper, Mn-Zn ferrite with a composition in which c is expressed by a positive value is termed the "conventional composition" (or "conventional Mn-Zn ferrite"). On the contrary, when c has a negative value and the composition number of Fe is less than 2, the material is referred to as "Fe-deficient composition" (or "Fe-deficient Mn-Zn ferrite") because the content of Fe is less than the stoichiometric composition.

Development of Mn-Zn ferrite for the 10 MHz range had been attempted with the conventional composition, but was not realized owing to the high relative permittivity, ε_r, of Mn-Zn ferrite with the conventional composition. The results of simulations showed that it is necessary to satisfy both high resistivity, ρ, and low ε_r simultaneously in order to improve the frequency characteristics of μ$_i$[2, 3]. Among these properties, high ρ can be realized relatively easily by adding grain boundary segregation additives such as $CaCO_3$, SiO_2, etc. to achieve high resistivity of the grain boundaries[4, 5]. However, substantial improvement in the frequency characteristics of μ$_i$ was difficult because this approach simultaneously increases ε_r.

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On the other hand, it is known that Fe-deficient Mn-Zn ferrite has a high ρ[6], and it has been reported that low ε_r can also be realized simultaneously in combination with high ρ[7–9]. Therefore, the authors investigated a high permeability Mn-Zn ferrite material with a Fe-deficient composition and obtained a Mn-Zn ferrite that maintains μ_i up to the 10 MHz range. However, it was found that this material has the problem called magnetic deterioration, that is, a large decrease in μ_i after a large magnetic field is applied.

First, this report describes the effect of selection of a Fe-deficient composition in improving the frequency characteristics of μ_i. Next, the cause of the magnetic deterioration that appeared as a result of the selection of the Fe-deficient composition is discussed, together with measures for its suppression. Finally, the various properties of the developed material are introduced.

2. Experimental

2.1 Sample Materials

The principal components Fe_2O_3, Mn_3O_4, ZnO and CoO were weighed, mixed and calcined. After adding $CaCO_3$ and SiO_2 to the obtained calcined powder, the mixture was pulverized and then granulated by adding aqueous solution of polyvinyl alcohol (PVA). Toroidal cores with an outer diameter of 31 mm, inner diameter of 19 mm and height of 7 mm were produced by compacting the granulated material at a pressure of approximately 100 MPa using a press and mold, followed by sintering under atmospheric control using an electric furnace.

For comparison with the properties of the developed material, samples of conventional Mn-Zn ferrite and Ni-Zn ferrite with the same geometry were also prepared. MA055 produced by JFE Ferrite by the actual commercial process was used as the conventional Mn-Zn ferrite, and a trial product with a composition of $Ni_{0.51}Zn_{0.50}Fe_{1.99}O_4$ was used as the Ni-Zn ferrite.

2.2 Evaluation Method

Initial permeability μ_i was measured using a sintered coil wound with 10 turns of copper wire (diameter: 0.40 mm). In accordance with JIS C 2561, in the range from 1 kHz to 1 MHz, μ_i was calculated from the inductance (L_S) measured using an LCR meter (Hewlett Packard, now Keysight Technologies; 4284A), and from 1 MHz to 40 MHz, μ_i was calculated from the complex impedance, Z and the phase angle, θ, measured using an impedance analyzer (same company, 4194A). The saturation magnetic flux density, B_m, and the residual magnetic flux density, B_r, were measured with a B-H tracer (Riken Denshi Co., Ltd.; BHS-40)

using cores wound 20 turns with copper wire (diameter: 0.60 mm) on the primary side (excitation side) and 40 turns on the secondary side (measurement side). The core was excited with a direct current, and the strength of the applied magnetic field was 1 200 A/m. DC resistivity was measured by the 4-probe method described in JIS C 2561, and surface resistance was measured in accordance with JIS C 2141. The contents of the main components and the constituent ions were all measured by titration method. The ε_r of the material was measured using a network analyzer (Hewlett Packard, now Keysight Technologies; 4285A) by a technique in accordance with JIS R 1627.

3. Results and Discussion

3.1 Properties of Fe-Deficient Mn-Zn Ferrite Trial Material

Figure 1 shows the frequency characteristics of μ_i of a Mn-Zn ferrite trial material (trial material A) produced with a Fe-deficient composition expressed by $Mn_{0.62}Zn_{0.40}Fe_{1.98}O_{3.99}$. Comparing the attenuation frequency, f_r, of μ_i of the sample materials, μ_i of MA055, i.e., the conventional Mn-Zn ferrite, shows sharp attenuation at around 1 MHz, while the Fe-deficient Mn-Zn ferrite, like the NiZn ferrite, maintains μ_i up to the 10 MHz region.

A comparison of the magnetic properties of the samples is shown in **Table 1**. Although the conventional
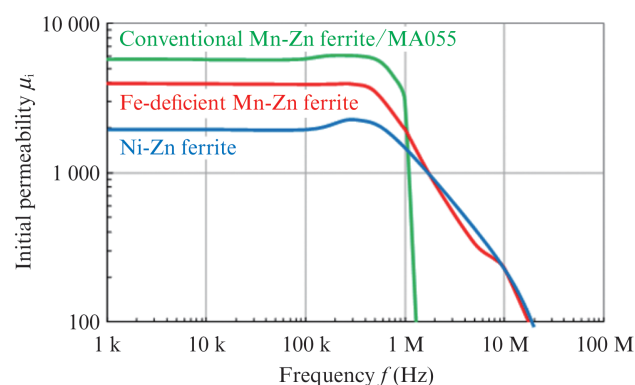

Fig. 1   Comparison of initial permeability vs frequency

Table 1   Comparison of magnetic properties of high-μ_i MnZn ferrite

	μ_i@10 kHz 23°C	f_r (MHz)	Fe^{2+} (mass%)	ρ(Ωcm)
Conventional MnZn ferrite	5 500～15 000	0.1～2	$\doteqdot$ 1～2	～10^2
Fe-deficient MnZn ferrite	1 300～2 200	～10	$\doteqdot$ 0	～10^6

Mn-Zn ferrite has a Fe^{2+} ion content of 1 to 2 mass%, the Fe^{2+} content is reduced to substantially 0 mass% when the Fe-deficient composition is selected. It is known that the presence of the Fe^{2+} ion in ferrite decreases resistivity by causing electron hopping with the Fe^{3+} ion [10]. Thus, an increase in ρ in trial material A is realized by decreasing the Fe^{2+} ion. The frequency characteristics of ε_r, which is a controlling factor for improvement of the high frequency characteristics of μ_i, are shown in **Fig. 2** in comparison with those of the other sample materials. Since the ε_r of trial material A decreases sharply at frequencies higher than 300 kHz, it is possible to suppress eddy current loss, which is the main factor in attenuation of μ_i in the high frequency region. As a result, it is thought that the frequency characteristics of μ_i were significantly improved, and μ_i could be kept up to the 10 MHz range.

Summarizing this discussion, these results showed that a simultaneous increase in ρ and decrease of ε_r can be achieved by selecting the Fe-deficient composition, and as a result, μ_i can be maintained up to the 10 MHz range.
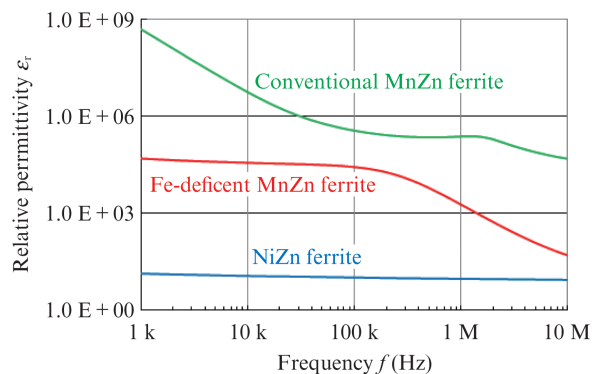
3.2 Saturation Magnetization Properties and Appearance of Magnetic Deterioration

Table 2 shows the DC magnetization properties of the conventional Mn-Zn ferrite and the Fe-deficient trial material A. In comparison with the conventional composition, the residual magnetic flux density B_r and B_r/B_m ratio of trial material A are approximately 4 times larger. The first quadrants of the B-H hysteresis loops of the conventional Mn-Zn ferrite and trial material A were extracted and compared, as shown in **Fig. 3**. In Fig. 3, the μ_i equivalent to the slope of the rise of the initial magnetization curve is shown by the dotted lines, and the magnetization current in the condition after magnetization (residual magnetization state) is shown schematically by the broken lines. Focusing on the difference between the initial magnetization curve and the magnetization curve after magnetization, in the case of the conventional MA055, which has a small B_r/B_m ratio, there is almost no difference in the slopes of the initial magnetization curve and the curve after magnetization, and for this reason, there is also no large difference between the μ_i after magnetization and in the demagnetized condition. In the case of trial material A, which has a large B_r/B_m ratio, the slope of the magnetization curve after magnetization decreases greatly compared with the initial magnetization curve. This means the value of μ_i decreases after magnetization in a large field, and is the

Fig. 2　Comparison of permittivity vs frequency

Table 2　Comparison of DC magnetization properties

	B_m (mT)	B_r (mT)	B_r/B_m	H_c (A/m)
Conventional MnZn ferrite	430	70	0.16	5
Fe-deficient MnZn ferrite	390	270	0.70	15

Fig. 3　Comparison of B-H hysteresis loops　a) conventional composition　b) Fe-deficient composition
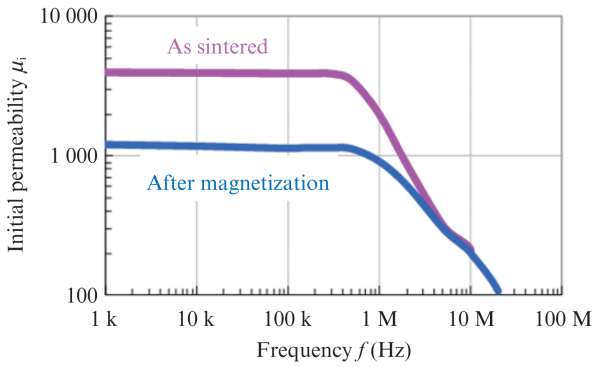
Fig. 4　Initial permeability of Fe-deficient MnZn ferrite before and after magnetization

phenomenon called magnetic deterioration.

Figure 4 shows a comparison of the frequency characteristics of μ_i for trial material A in the initial magnetization state and in the residual magnetization state after saturation magnetization by the magnetic field application of 1 200 A/m. The value of μ_i at 1 kHz is around 4 000 in the initial magnetization state, but deteriorates by as much as 70 %, to approximately 1 200, after magnetization.

Supposing a condition in which the trial material is used in a noise filter, which is its main application, there is a possibility that a large pulse current or surge current may flow through the filter. In this case, a large field will be applied to the filter core, resulting in a residual magnetization state after the current has passed. To maintain the designed function of the filter even after this kind of magnetization, it is necessary to keep substantially the same μ_i as in the demagnetized state in the material even after magnetization. Thus, for commercialization as a practical material, the value of

the B_r/B_m ratio must be reduced to the same level as that of the conventional composition.

3.3 Control of Magnetocrystalline Anisotropy by CoO Substitution

In ferromagnetic materials, the area and B_r/B_m ratio of the *B-H* hysteresis loop are generally large in the case of hard magnetic materials and, conversely, are small in soft magnetic materials[11]. Although a soft magnetic property are required in Fe-deficient Mn-Zn ferrite, trial material A displayed a hard magnetic property, as described in the previous section. Since the difference between hard and soft magnetic properties is due to the anisotropy of the material, we attempted improve the performance of the Fe-deficient material by focusing on its magnetocrystalline anisotropy.

Figure 5 shows schematic diagrams of the temperature dependence of magnetocrystalline anisotropy and μ_i of the conventional composition and the Fe-deficient composition. As shown in Fig. 5 a), among the metallic ions in the conventional material, only Fe^{2+} has a positive magnetocrystalline anisotropy constant, K_1, and the K_1 of Fe^{3+} and Mn^{2+} is negative. The summation of the total magnetocrystalline anisotropies of the Mn-Zn ferrite is represented by the dotted line in the figure, and there is a temperature where $|K_1|=0$ [12].

Here, μ_i is expressed as a function of K_1 as shown in Eq. (1) [13].

$$\mu_i \propto \frac{Ms^2}{|aK_1 + b\lambda\sigma|} \quad\cdots\cdots\cdots\cdots\cdots\cdots\cdots (1)$$

(*M*s: saturation magnetization, λ: magnetostriction constant, σ: stress, *a*, *b*: constants)
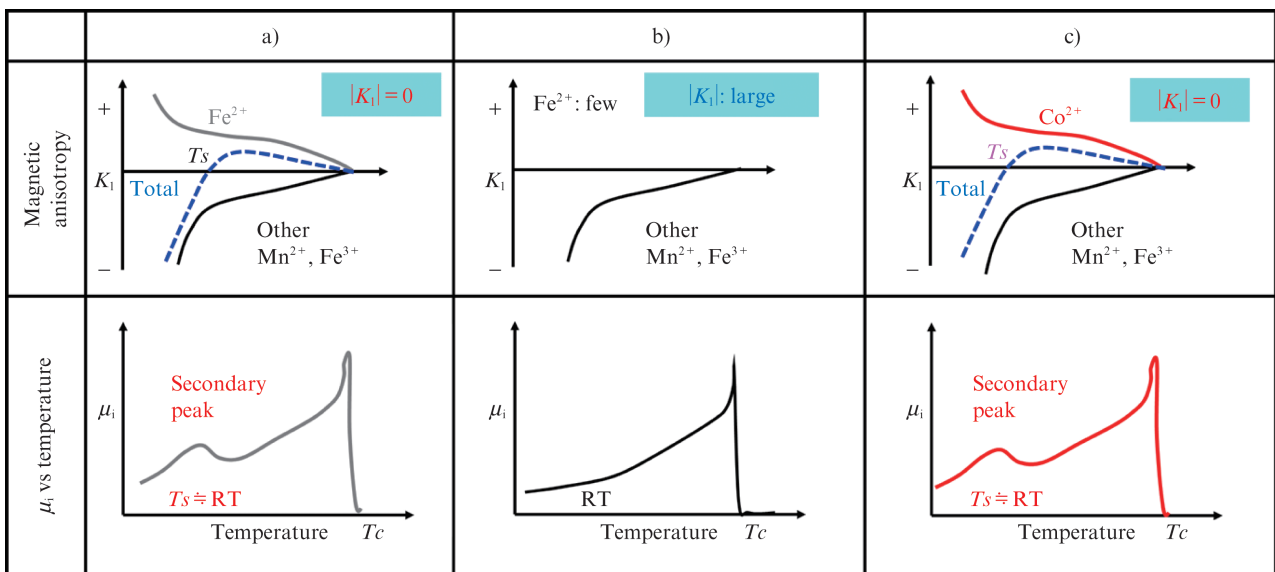

Fig. 5　Schematic diagrams of temperature dependence of magnetic anisotropy and initial permeability
a) conventional composition, b) Fe-deficient composition, c) Fe-deficient composition with CoO substitution
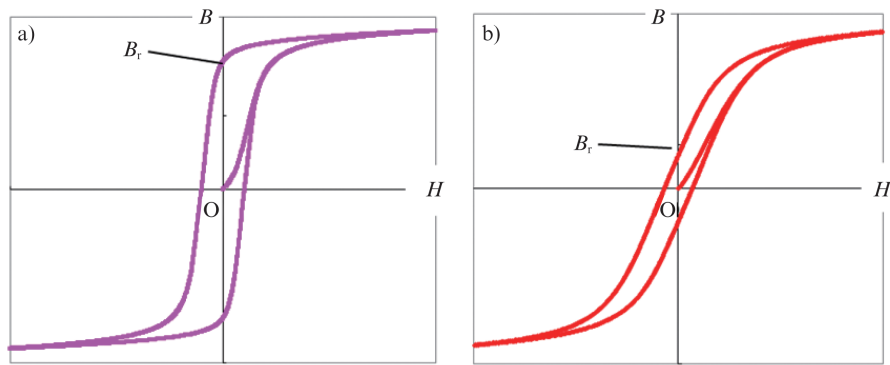
Fig. 6   *B-H* hysteresis loops of Fe-deficient MnZn ferrite: a) without CoO substitution, b) with CoO substitution

μ_i displays a local maximum value, called the secondary peak, at the temperature where $|K_1|=0$. To obtain a higher μ_i in high permeability materials, including MA055, the composition design and sintering conditions are arranged so that the secondary peak appears at around room temperature[3]. Magnetic deterioration necessarily does not occur around room temperature because both $|K_1|$ and the B_r/B_m ratio are small.

However, as shown in Table 1 and Fig. 5 b), the trial material with the Fe-deficient composition, unlike the material with the conventional composition, contains substantially no Fe^{2+} ions, which have positive values of K_1. Therefore, it can be inferred that the Fe-deficient material consists of only components with negative values of K_1, and the B_r/B_m ratio is large because $|K_1|$ increases at around room temperature. Moreover, the fact that a point where $|K_1|=0$ does not exist near room temperature also supports the conclusion that a secondary peak does not exist in the temperature dependency of μ_i shown in Fig. 5 b).

In order to reduce $|K_1|$ at near room temperature while maintaining the good frequency characteristics of the trial material, it is necessary to add a component other than the Fe^{2+} ion which has a positive K_1.

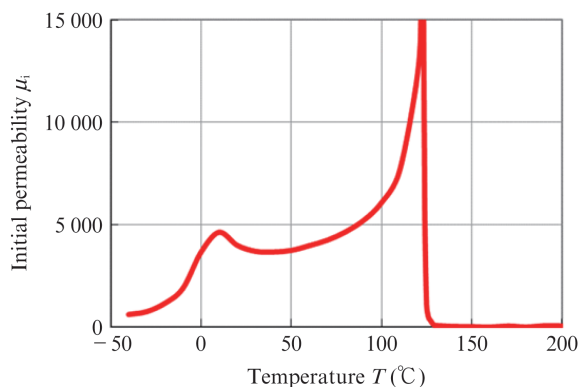Here, we focused on the Co^{2+} ion, as this ion has a positive K_1. In the past, JFE Ferrite developed a Mn-Zn ferrite material with low iron loss over a wide temperature range by adding the Co^{2+} ion to control K_1, and commercialized that material under the name MBT1[12].

Similarly, in the developed material, the aim was to realize $|K_1|=0$ at around room temperature, as shown in the example in Fig. 5 c), by using partial substation of CoO to control K_1. Moreover, if it was possible to realize $|K_1|=0$, the appearance of a secondary peak in the temperature characteristics of μ_i similar to that in Fig. 5 a) was expected.

3.4 Magnetic Deterioration Suppression Effect of CoO Substitution

Figure 6 shows a comparison of the *B-H* hysteresis loops of the Fe-deficient trial material A without CoO substitution, and a trial material (trial material B) in which CoO was substituted for 1.7 mol% of the main components. As shown in Fig. 6 b), B_r decreased as a result of CoO substitution, and a loop with a soft magnetic shape like that of the conventional Mn-Zn ferrite was obtained. **Figure 7** shows the temperature dependence of μ_i of trial material B. A secondary peak appeared accompanying CoO substitution, and it is conjectured that this occurred because $|K_1|=0$ was realized at around room temperature, as in the case of the conventional composition. **Table 3** shows the B_r/B_m ratio and magnetic deterioration ratio without/with

Fig. 7   Temperature dependence of initial permeability of Fe-deficient composition with CoO substitution

Table 3 B_r/B_m and magnetic deterioration ratio[*], compared Fe-deficient MnZn ferrite with and without CoO substitution

	B_r/B_m	Magnetic deterioration ratio[*]
Without CoO substitution	0.70	0.70
With CoO substitution	0.23	0.02

[*] Decline of μ_i after 1.2 kA/m magnetization per before magnetization

CoO substitution. The magnetic deterioration ratio was greatly reduced by reduction of the B_r/B_m ratio.

As described above, this research clarified the fact that magnetic deterioration can be suppressed by reducing the B_r/B_m ratio, which was accomplished by partial substitution of CoO in the composition to compensate for positive/negative magnetocrystalline anisotropy at near room temperature.

3.5 Magnetic Properties of Developed Material (MR04)

The problems related to mass production were solved by JFE Ferrite, and the developed material was commercialized under the name "MR04." **Figure 8** shows a comparison of the frequency dependence of initial permeability μ_i of MR04 and the conventional Mn-Zn ferrite MA055 and NiZn ferrite. MR04 maintains, μ_i, up to the 10 MHz range even after CoO substitution to suppress magnetic deterioration. Comparing these three materials, the μ_i of MR04 is superior to that of the conventional Mn-Zn ferrite at frequencies of 1 MHz and higher, and is also superior to the μ_i of NiZn ferrite in the kHz region. **Table 4** shows the magnetic properties of MR04 and the comparison materials. In comparison with NiZn ferrite, MR04 has a higher Curie temperature and higher magnetic flux density. Based on these results, it can be said that MR04 is a superior material which is advantageous for downsizing of components, and can also be used in the magnetic cores of noise filters operating under high temperature environments in automotive applications, etc.
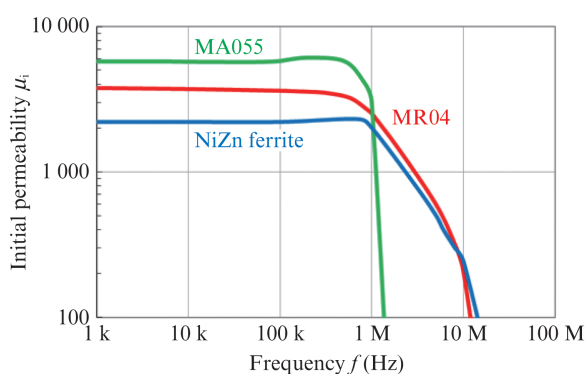
4. Conclusion

A new type of high resistance Mn-Zn ferrite was developed by focusing on a Fe-deficient composition, and the following results were obtained.

(1) A Mn-Zn ferrite material which maintains initial permeability, μ_i, up to the 10 MHz range was obtained by selecting a Fe-deficient composition. However, the material displayed so-called magnetic deterioration, as μ_i deteriorated by 70 % in the residual magnetization state in comparison with μ_i in the initial state.

(2) The estimated cause of this magnetic deterioration phenomenon was the composition of the Fe-deficient Mn-Zn ferrite, which comprised only metallic ions with negative magnetocrystalline anisotropy. Therefore, magnetic deterioration was successfully suppressed while maintaining μ_i up to the 10 MHz range by partial substitution of CoO, which has positive magnetocrystalline anisotropy.

(3) The developed material has now been commercialized by JFE Ferrite Co., Ltd. under the name MR04. Because MR04 has a higher μ_i, higher Curie temperature and higher magnetic flux density than the conventional NiZn ferrite, downsizing of parts and use under high temperature environments are possible. Thus, the new product is suitable for the magnetic cores for automotive noise filters.

Fig. 8 Frequency dependence of initial permeability of MR04 and conventional materials

Table 4 Magnetic properties of MR04 and high-μ_i conventional materials

		μ_i@10 kHz, 23°C	f_r (MHz)	T_c (°C)	B_m (mT)
MR04	Developed	3 800	～10	120	380
MA055	Conventional	5 500	～2	140	430
NiZn	Conventional	2 000	～10	110	270

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