BNL-105227-2014-TECH

Booster Technical Note No. 183;BNL-105227-2014-IR

OBSERVATION of INDUCED ELECTRICAL CONDUCTIVITY of KICKER MAGNET FERRITES, AFTER VACUUM FIRING

M. A. Goldman

November 1990

Collider Accelerator Department

Brookhaven National Laboratory

U.S. Department of Energy

USDOE Office of Science (SC)

DISCLAIMER

OBSERVATION of INDUCED ELECTRICAL CONDUCTIVITY of KICKER MAGNET FERRITES, AFTER VACUUM FIRING

BOOSTER TECHNICAL NOTE
NO. 183

M. A. GOLDMAN and J. E. TUOZZOLO

NOVEMBER 8, 1990

ALTERNATING GRADIENT SYNCHROTRON DEPARTMENT
BROOKHAVEN NATIONAL LABORATORY
UPTON, NEW YORK 11973

Observation Of Induced Electrical Conductivity Of Kicker Magnet Ferrites, After Vacuum Firing

M.A. Goldman and J.E. Tuozzolo
November 1, 1990

ABSTRACT

The kicker magnets for the AGS Booster synchrotron are to be operated in an ultra-high vacuum environment, and must not serve as sources of residual gas. After vacuum bakeout of a magnet's ferrite core block at 900° C, and a bakeout of a second core block at 550° C, it was observed that the blocks had become electrically conductive and thereby unsuitable for magnet use.

Baking of the ferrite in vacuum apparently led to induced electrical conductivity. To verify whether this was, in fact, the case and, if so, to determine acceptable bakeout times and temperatures, small toroidal ferrite samples were baked under vacuum for a variety of bakeout times and temperatures. Their bulk radiofrequency electrical resistivity and permittivity were measured subsequently. For the CERMAG 5005 material used, induced conductivity was observed when the bakeout temperature was 500° C or greater, the conductivity increasing with increasing bakeout temperature. At 400° C no increase in conductivity was observed. Measurements of magnetic permeability and ferrite figure of merit (μQf product) of the toroid baked at 400° C showed minor changes in the values of these parameters, compared with an unbaked toroid, but showed no essential degradation.

These results are discussed in relation to the well-known sensitive dependence of electrical resistivity of nickel-zinc ferrites upon stoichiometry, and whether the ferrites are of iron-excess or deficiency type. A maximum vacuum bake temperature of 400° C is suggested.

1. Introduction.

The design of the AGS Booster synchrotron incorporates kicker magnets for beam injection, extraction, and instrumentation. These magnets are located within the vacuum envelope of the beam, and they will have to operate in an ultra-high-vacuum environment. They must not act as virtual gas leaks. Their outgassing must be minimal, to prevent electron capture and beam scattering, effects which are particularly pronounced when accelerating highly ionized heavy ions.

The fast rise times required for the kicker magnets are obtained by use of ferrite magnet cores. The cores are made of nickel-zinc-spinel type ceramic of high resistivity and high permeability. They are manufactured by pressing and air firing of the powdered ceramic. Although cores close to full density are produced, a residual porosity remains. For this reason, the cores are fired in an ultra-high-vacuum furnace before installation in the Booster and are baked subsequently at 300° C under vacuum after installation in the Booster ring.

The material used for the cores is Ceramic Magnetics,Inc. type CMD5005 nickel-zinc ferrite, containing 49.8 mole percent Fe_2O_3, and prepared from 99.99% purity ingredients; no dopant or additive is used. A ratio near 35 NiO/65 ZnO is used. In order to reduce outgassing it was proposed, initially, that the cores be fired under vacuum at 900° C for four hours. Blocks fired to this schedule came out of the furnace with a surface discoloration. A check of their dc resistivity, with a digital voltmeter, showed a resistivity of 21,000 ohm-cm. An attempt made to "Hi-Pot" the blocks was unsuccessful. These tests, when made on unfired blocks, showed no measurable conductivity, and the unfired blocks were hi-potted to 15 kV.

This indicated a significant problem, because the magnet designs exploit the ferrite's excellent insulating properties, by using the ferrite core to support the magnet coils. Some of the magnets must operate at 26 kV.

At first it was conjectured that free zinc, because of its high vapor pressure, had diffused from the ferrite and condensed on the surface, causing the discoloration. But an Auger Analysis of the ferrite indicated that there was no more zinc on the surface than in the bulk of the ferrite. Removal of the surface discoloration by bead blasting was also tried. The measured resistivity increased by an order of magnitude, but the improvement was not enough to allow hi-potting above 350 volts.

When additional ferrite blocks were fired in vacuum at 550° C, appreciable D.C. conductivity was also observed.

To examine the effect of vacuum bakeout on the electrical properties of the ferrite material, a number of small toroidal cores were baked in vacuum at temperatures up to 600° C. Their radiofrequency conductivity and dielectric permittivity were measured subsequently, over the frequency range from 0.5 to 5.0 MHz. The permittivity of high resistivity nickel-zinc ferrites is constant in this frequency range. It is expected that an appreciable increase in bulk electrical conductivity of the ferrite will be accompanied by dispersive permittivity, that is, an induced variation of permittivity with respect to frequency; its presence is evidence of bulk conductivity. Rings baked at 500, 550 and 600° C showed induced conductivity. Unbaked rings and rings baked at 250, 300 and 400° C did not. This suggests that the maximum allowed bakeout temperature should lie between 400 and 500° C. To see if a vacuum bake at 400° C would change the magnetic properties of a core, a second sample was given a 50 hour bake at this temperature. The magnetic permeability and figure of merit were measured, and compared to those of an unbaked sample; permittivity and resistivity were also measured.

2. Method Of Measurement.

The rings under test were cylindrical toroids, of nominal length 0.500", outer diameter 0.867", inner diameter 0.538", each dimension ground constant to ±0.001". To carry out the permittivity and resistivity measurements after bake, the plane end surfaces of each ring were painted with conducting silver-epoxy cement (Epo-Tek H20, Epoxy Technology Inc., Billerica, Mass.). Annular electrode rings were cemented onto these ends to form a cylindrical capacitor; care was taken that the conductive cement did not contact the cylindrical ring surface. The complex impedance of the capacitor was measured on a Hewlett-Packard type HP 4815A vector voltmeter, over the frequency range 0.5 to 5.0 MHz. Electrode lead lengths were kept short.

The impedance $Z = |Z| \exp(j\theta)$ of the ferrite capacitor is represented by that of a parallel combination of an ideal capacitor of capacitance $C = \epsilon' A/d$ and an ideal resistor $R = d\rho/A$ so that $1/Z = jwC + 1/R$. (Alternatively, the capacitor can be represented by an ideal capacitor with a complex dielectric coefficient $\epsilon = \epsilon' - j\epsilon''$, where $\omega\epsilon'' = \sigma$). The real permittivity and resistivity, which are in general frequency-dependent quantities, are obtained from the measured $|Z|$ and θ from the relations

$$\sigma = 1/\rho = A\,|Z|\,\sec(\theta)\,/\,d,$$
$$\epsilon'/\epsilon_0 = d \sin(-\theta)/A\omega\,|Z|,$$

where A is the ferrite end face area and d is the ferrite length.

Magnetic measurements were made on a ferrite ring sample vacuum baked for fifty hours at 400° C, after it was found that a sample baked at that temperature for twelve hours showed no measured conductivity or dispersion in permittivity. Initial permeability and figure of merit were measured in order to see if significant changes occurred in these magnetic properties during the bake and to see if the magnetic properties of a ferrite baked to this schedule were still suitable for kicker magnet application. A long vacuum bake could possibly lead to grain growth in the sample which, for undoped nickel-zinc material, could cause increased permeability and larger magnetic loss.

For these measurements the bare ring sample was wound as a three-turn toroidal inductor. Complex impedance of the inductor was measured on the HP 4815A vector voltmenter. The sample is sufficiently small that frequencies of possible dimensional resonance are high compared to measurement freqencies; series lead resistance and interturn capacitance are small. A lossy inductor may be represented by either a parallel or a series circuit model; here we use a parallel combination of an inductor L_p and a resistor R to describe the inductor. The real and imaginary impedance components are measured, in order to define a "parallel" complex permeability, by the equations $Lp = Lo\mu'_p$ and $R = \omega L_0 \mu''_p$, where $L_0 = n^2 \mu_0 (d/2\pi) \ln(r_0/r_i)$ is the inductance of n turns on an identical core of unit permeability, outer radius r_0, inner radius r_i, and length d. These components of complex permeability are material properties, and should be independent of the number of turns and size of core.

(The use of parallel complex permeability for characterization of ferrites has been studied experimentally by Watson and Amoni [1] and is discussed in some detail in their paper, including a comparison with the more usual series representation of complex permeability (which does not give a permeability independent of core construction). These authors found that the parallel permeability components are each monotonic-decreasing functions of frequency, in contrast to the usual series components; in the present measurements this was found also to be the case).

The quality factor, Q, of the ferrite is, in the parallel representation:

$$Q = R/\omega L_p = u''_p/\mu'_p,$$

and depends upon the material and frequency but not upon the inductor's geometry. The quantity $u'_pQf = u''_pf$ can be considered to be a figure of merit of the material, in the fol-lowing sense. When an inductor of given core shape and number of turns is excited at frequency f by an rms voltage V at its terminals, the peak a-c flux density in the core is determined by Faraday's induction law and is independent of the core material. The magnetic power loss in the core is V^2/R. But, from the definitions above, we have

$$R = (2\pi L_0)(\mu'_p\, Qf)$$

and the loss is inversely proportional to the u'_pQf product of the core material when core shape, number of turns, frequency and operating voltage (or flux density) are specified.

3. Measurement Results.

Results of the measurements are shown in Figures 1 to 4. The ring baked at 600° C shows both appreciable conductivity and dispersive permeability below 1.5 MHz, compared to an unbaked ring and one baked at 400° C. The permittivities of the latter two rings show little variation with frequency and are close to one another. The ring baked at 400° C shows approximately 20% higher permeability than the unbaked ring and shift of position of the shoulder of the permeability versus frequency curve, and shows a minor decrease in the figure of merit over part of the measured frequency range. Our interpretation of these observations is discussed later in this note.

The ring bakeout schedules and measured resistivities are tabulated below:

Bake Temperature (Degrees C)	Vacuum Bake Time (Hours)	Measured Resistivity (Ohm-Centimeters)
Unbaked		$\rho > 10^7$
250	50	$\rho > 10^7$
300	200	$\rho > 10^7$
400	12	$\rho > 10^7$
400	50	$\rho > 10^7$
500	24	$5 \times 10^5 < \rho < 2 \times 10^6$
550	12	$1.7 \times 10^5 < \rho < 2.2 \times 10^5$
600	24	$2.0 \times 10^4 < \rho < 2.4 \times 10^4$

4. Discussion Of Results.

The unbaked ferrite and rings baked up to 400° C showed high resistivity; rings baked above 500° C showed decreasing resistivity as bake temperature increased. The ring baked at 600° C showed a resistivity of 22,000 ohm-cm, constant over the 0.5 to 5.0 MHz frequency range. The unbaked and 400C/50Hr rings showed a non-dispersive relative permittivity of 34.5 ± 1 over this range. The 600C/24Hr ring showed increasing permittivity as frequency decreased below 1.5 MHZ (Fig.1). Dispersion in permittivity with increased permittivity at low frequency is characteristic of iron-excess ferrites, which are semiconductors; in contrast to iron-deficiency ferrites, which are insulators.

The electrical resistivity of nickel-zinc spinel ferrites is strongly dependent on whether the iron content of the material is in excess or is in deficit of the stoichoimetric content [2, 3]. (An abrupt change, of 4 to 6 orders of magnitude, can occur when the Fe_2O_3 content increases by 0.2 mole percent [3] across this threshold). These ferrites are normally made with a composition which is only slightly iron deficient, in order to reduce loss caused by magnetostrictive effects and to increase permeability. In deficiency-type material, which is highly resistive, all of the iron is in a trivalent (ferric) state; half of the iron lies on tetrahedral lattice sites, the other half on octahedral sites. The divalent nickel and zinc ions lie on the remaining octahedral sites. In excess-type material, some of the nickel or zinc ions are replaced by divalent (ferrous) iron, and iron is found in both divalent and trivalent form on crystallographically equivalent sites. Conduction by hopping of electrons from ferrous to ferric sites is then possible [2].

When the ferrites are heated in vacuum, oxygen leaving the surface is not replaced. This suggests a cause for the induced conductivity. Due to activation during heating, oxygen is able to percolate or diffuse from internal pore sites or grain boundary sites to the surface, where it is lost. Local iron sites neighboring to these internal sites convert to ferrous sites on departure of oxygen. Conduction is then possible. Neither bulk dissociation of the ferrite nor zinc evaporation is required to produce iron-excess regions by this mechanism; it is known, in fact, that zinc evaporation from these ferrites is low below a temperature of 1000° C, [2], and dissociation pressures of metal oxide components, from which the ferrite is formed, are low in this range [4]. The thermal activation energy required to remove oxygen from internal pore surface sites is less than the energy required to remove oxygen from sites in the interior of of the bulk material, and conduction at the relatively low temperature of 500° C becomes possible.

Our model suggests the following behavior of the ferrite under vacuum bake. The number of lattice sites available for conduction will grow rapidly with temperature because of the increased rate at which oxygen ions leave sites on internal pore surfaces; the actual rate of removal of removal of oxygen from the material will be controlled by diffusion or percolation of oxygen to the outer surface, where the oxygen is permanently removed.

At 400° C the activation and removal of oxygen from the ferrite does not yet appear significant. At 500° evidence of conductivity appears; by 600° short bake times are sufficient to produce significant conductivity. It is likely that high conductivity will be produced with short bake times at higher temperatures.

The real permeability versus frequency curve of the unbaked ring sample is quite typical for the material used. The combination of higher permeability and change of shape of the curve, taken together with the somewhat lower μQf product at low frequencies, for the sample fired at 400° C for 50 hours, suggests that some grain growth may have occurred in that sample during the vacuum firing. There is no major change in magnetic quality of the sample. Based on these results and a lack of observed conductivity, it seems likely that a vacuum bake of 400° C for one or two days will not damage the ferrite. Since there is, however, some sign of change in magnetic parameters at this temperature, one should be cautious about going to higher bake temperature; certainly 500° C is too high a temperature. The magnet core cycle of vacuum bakeout at 400° C followed by a subsequent vacuum bakeout at 300° C after installation into the Booster should be sufficient to allow pump-down to the required vacuum.

Acknowledgement

The authors wish to thank Kimo M. Welch for helpful discussions concerning the thermal stability and vacuum dissociation presures of metal oxides.

References

1. J.K. Watson and S. Amoni, Using Parallel Complex Permeability for Ferrite Characterization, IEEE Trans. MAG-25, 4224-4226 (1989).

2. L.G. Van Uitert, dc Resistivity in the Nickel and Nickel Zinc Ferrite System, J. Chem. Physics 23, 1883-1887 (1955).

3. F.G. Brockman and K.E. Matteson, Nickel-Zinc Ferrites: II, Preparation and Properties of Stoichiometric 32NiO/68ZnO Ferrite, J. Amer. Ceram. Soc.54,180-183 (1971).

4. E.L. Simons, Dissociation Pressures of Oxides, Hydrides and Nitrides, article in S. Dushman, Scientific Foundations of Vacuum Technique, 2nd Ed., John Wiley & Sons, New York, 1962.

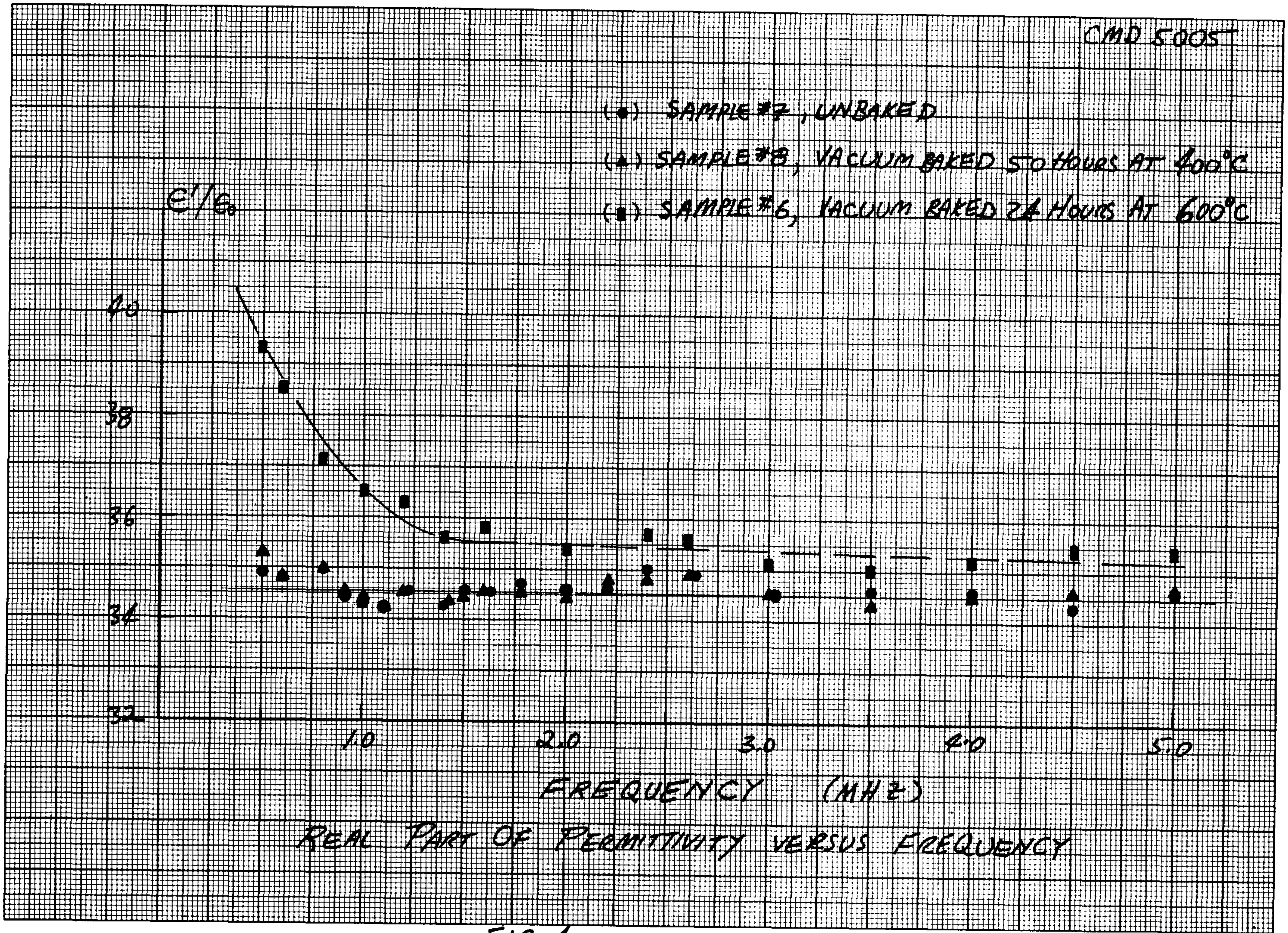
CMD 5005
(●) SAMPLE #7, UNBAKED
(▲) SAMPLE #8, VACUUM BAKED 50 HOURS AT 400°C
(■) SAMPLE #6, VACUUM BAKED 24 HOURS AT 600°C
ε'/ε₀
40
38
36
34
32
1.0
2.0
3.0
4.0
5.0
FREQUENCY (MHZ)
REAL PART OF PERMITTIVITY VERSUS FREQUENCY

FIG. 1

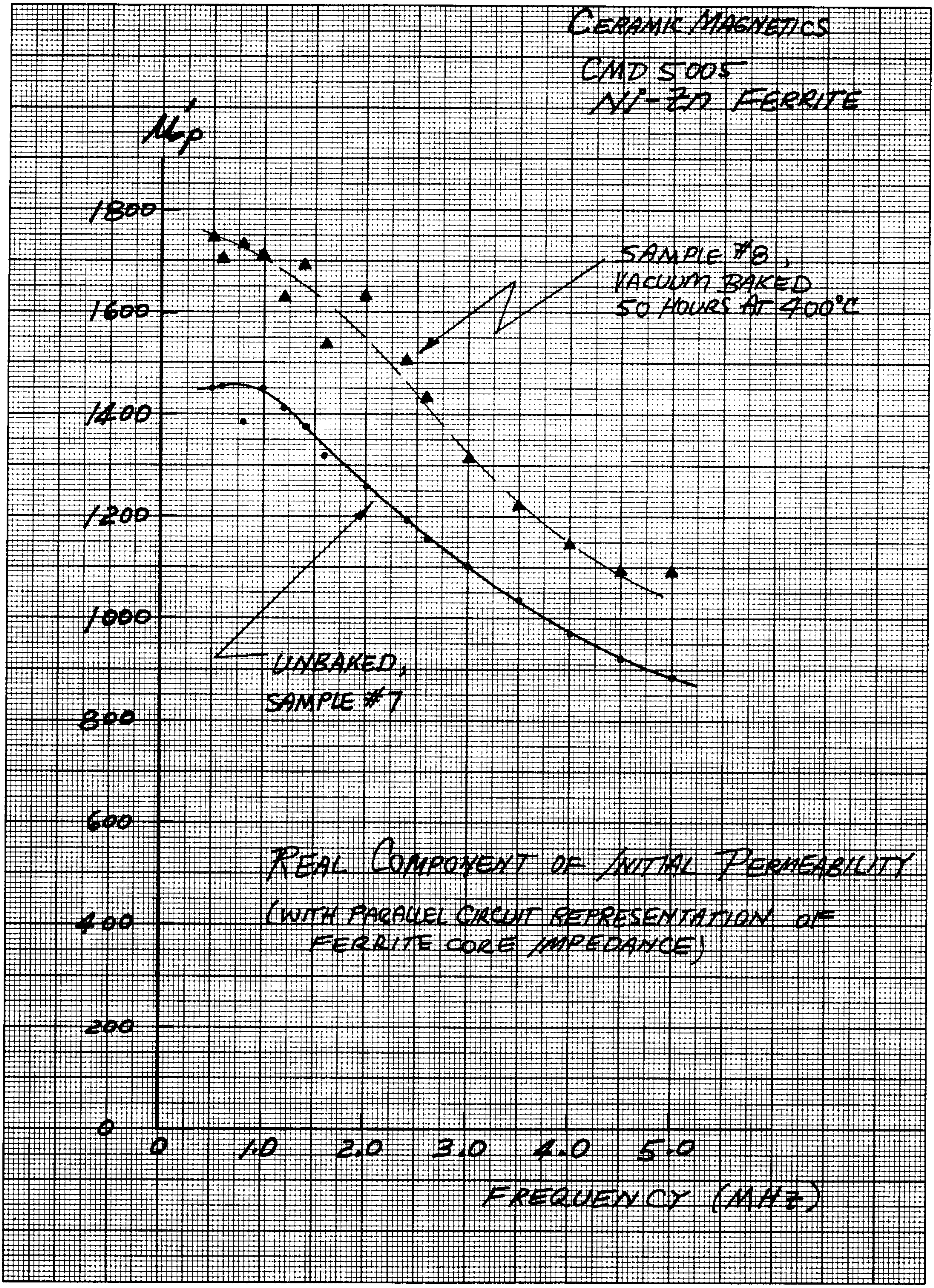
CERAMIC MAGNETICS
CMD 5005
Ni-Zn FERRITE
μ'p
1800
1600
1400
1200
1000
800
600
400
200
0
SAMPLE #8,
VACUUM BAKED
50 HOURS AT 400°C
UNBAKED,
SAMPLE #7
REAL COMPONENT OF INITIAL PERMEABILITY
(WITH PARALLEL CIRCUIT REPRESENTATION OF
FERRITE CORE IMPEDANCE)
0
1.0
2.0
3.0
4.0
5.0
FREQUENCY (MHz)

FIG. 2

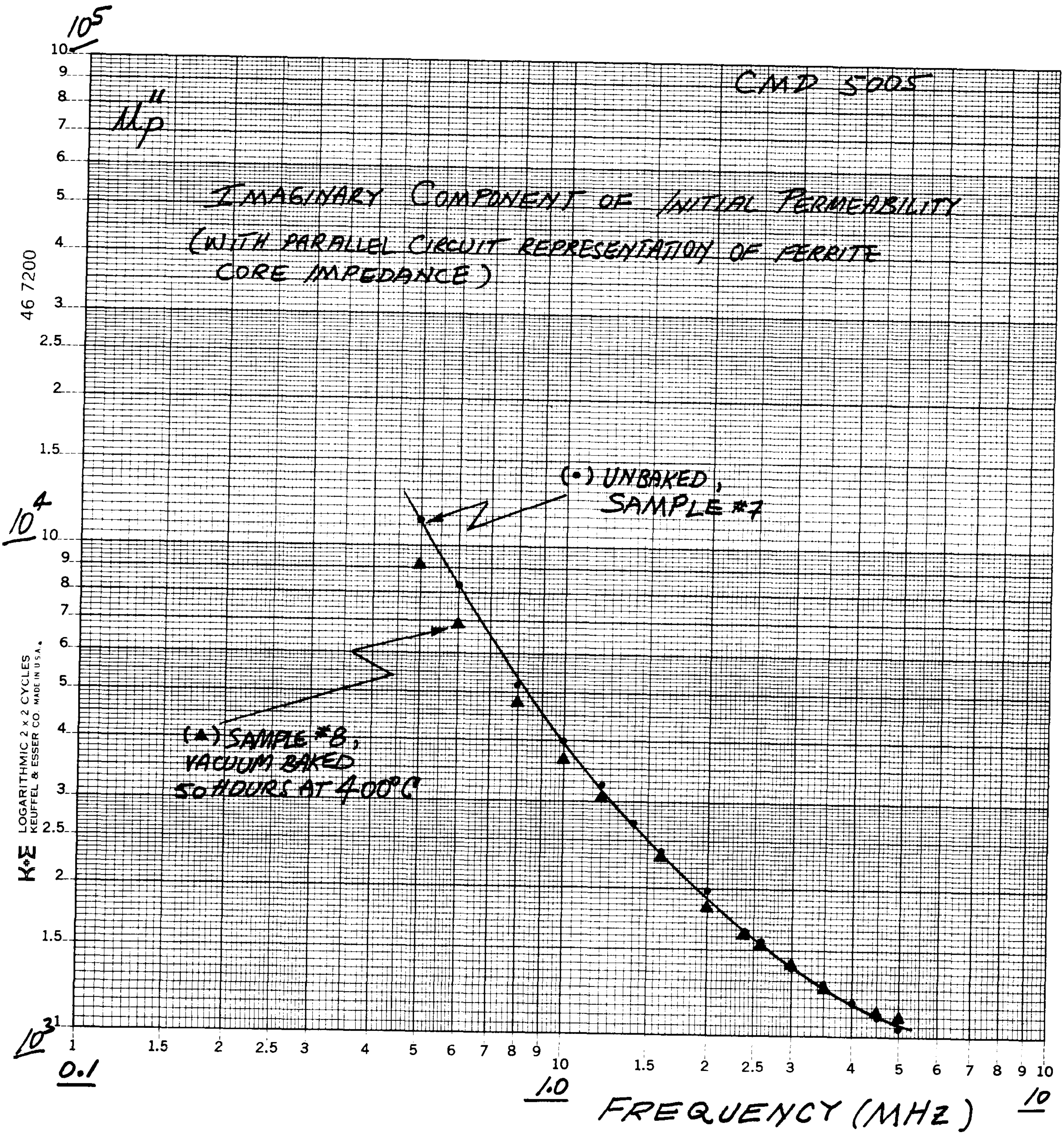
CMD 5005
IMAGINARY COMPONENT OF INITIAL PERMEABILITY
(WITH PARALLEL CIRCUIT REPRESENTATION OF FERRITE CORE IMPEDANCE)
μ_p''
(•) UNBAKED, SAMPLE #7
(▲) SAMPLE #8, VACUUM BAKED 50 HOURS AT 400°C
FREQUENCY (MHz)
0.1
1.0
10
10^3
10^4
10^5
46 7200
K+E LOGARITHMIC 2 x 2 CYCLES KEUFFEL & ESSER CO. MADE IN U.S.A.

FIG. 3

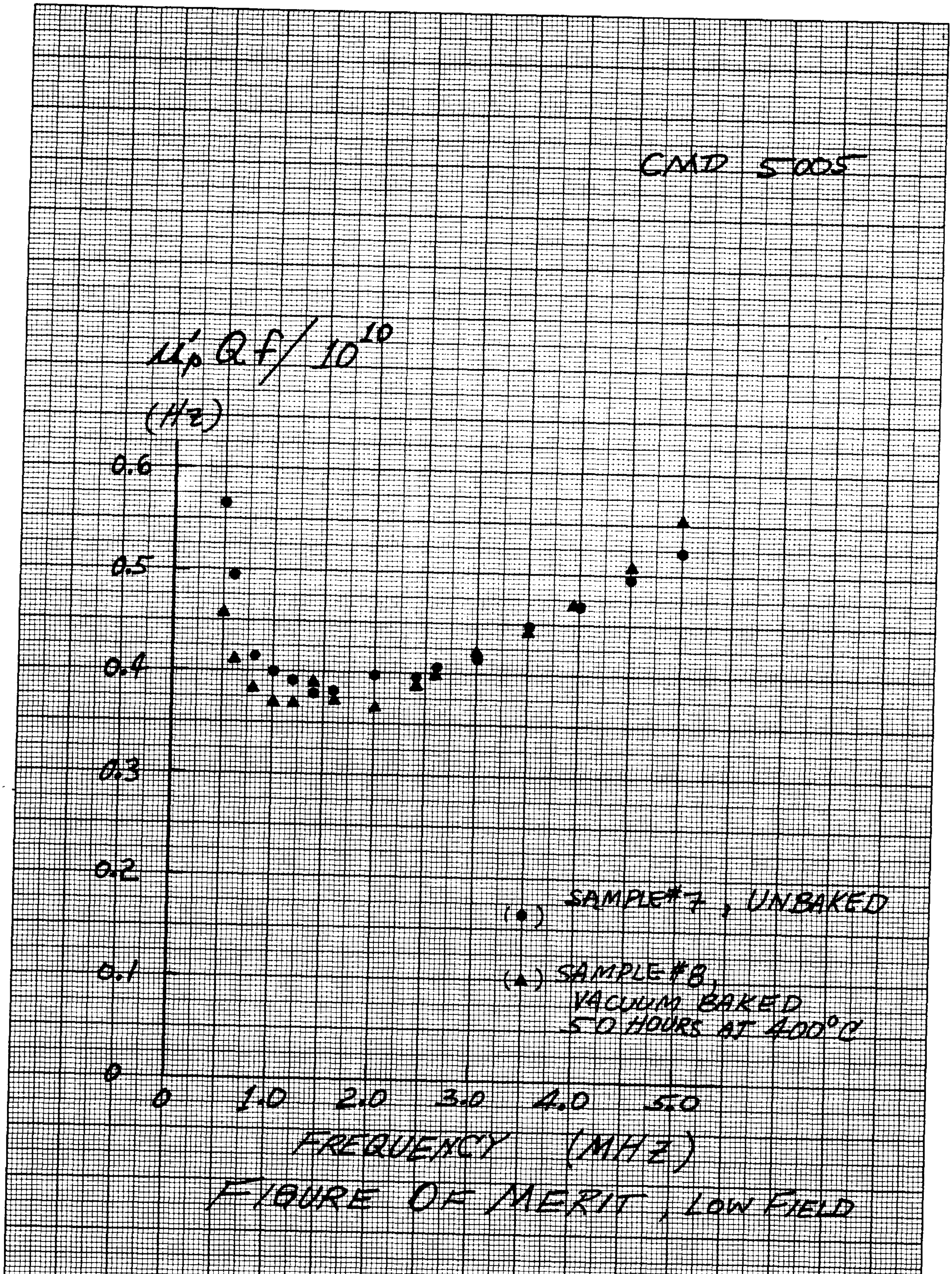
CMD 5005
μ'p Q f / 10^10
(Hz)
0.6
0.5
0.4
0.3
0.2
0.1
0
0
1.0
2.0
3.0
4.0
5.0
FREQUENCY (MHZ)
FIGURE OF MERIT, LOW FIELD
(●) SAMPLE #7, UNBAKED
(▲) SAMPLE #8, VACUUM BAKED 50 HOURS AT 400°C

FIG. 4

FERRITE DIELECTRIC MEASUREMENT

OBSERVER MAG   SHEET NUMBER 6-1

DATE 8/16/90   FERRITE RING I.D. 0.538×2.54 cm (di)

MFR CERAMIC MAGNETICS   RING O.D. 0.864×2.54 cm (do)

MATERIAL CMD 5005 SAMPLE #6   SINGLE RING HEIGHT 0.503×2.54 cm (h)

VACUUM BAKED 600° C 24 HOURS

$$\epsilon' = \frac{2{,}289\times10^{3}\,[\sin(-\theta)]}{(f/1\,MHz)(|Z|/1\,Ohm)\cdot G}$$

$$G = \frac{\left(\frac{d_o}{1cm}\right)^2-\left(\frac{d_i}{1cm}\right)^2}{(h/1cm)} = 2.308$$

$$\rho = \frac{4}{\pi}\frac{|Z|}{G\cos\theta} = \frac{1.2732\,|Z|}{G(\cos\theta)}$$

$$\delta_\epsilon = \pi/2+\theta \qquad \left(-\frac{\pi}{2}<\theta<0,\; 0<\delta_\epsilon<\pi/2\right)$$

$$\epsilon'' = \epsilon' \tan\delta$$

Vector Impedance Meter HP 4815A BNL # 100043

T (°C)	f MHz	Z Ohms	θ Degrees	sin(-θ)	δ_ϵ	Tan δ_ϵ	ε'	ε''	ρ Ohm-cm
27	0.5	31,400	-38.5	.6225			39.3		22,100
	0.6	29,100	-42.7	.6782			38.5		21,800
	0.8	25,400	-49.5	.7604			37.1		21,600
	1.0	22,400	-55.5	.8241			36.5		21,800
	1.2	19,600	-59.5	.8616			36.3		21,300
	1.4	17,800	-63.5	.8949			35.6		22,000
	1.6	15,700	-65	.9063			35.8		20,500
	2.0	13,150	-70	.9397			35.4		21,200
	2.4	11,070	-73	.9563			35.7		20,900
	2.6	10,300	-74	.9613			35.6		20,600
	3.0	9130	-76	.9703			35.1		20,800
	3.5	7950	-79	.9816			35.0		23,000
	4.0	6930	-80	.9848			35.2		22,000
	4.5	6130	-81	.9877			35.5		21,600
	5.0	5550	-82.5	.9914			35.4		23,500
		Est (±200)	Est (±0.5°)						

Use 3" short test leads