

# Dependence of magnetic properties of Mn–Zn ferrites on the degree of calcination

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$Mn_{0.764} Zn_{0.187} Fe_{2.049} O_4$  and  $Mn_{0.687} Zn_{0.272} Fe_{2.041} O_4$  ferrites containing 0.05 wt% CaO, 0.05 wt%  $SnO_2$  and 0.05 wt%  $V_2O_5$  were prepared by conventional methods using manganite ( $\gamma$ - $MnOOH$ ) as a source of MnO. The partial-calcined ferrites were made by calcining the mix consisting of total amount of ZnO and one third or half amount of  $Fe_2O_3$  and MnO required for the formation of the Mn–Zn ferrites and sintering the mix consisting of the previously calcined mix and the remaining two thirds or half the amount of  $Fe_2O_3$  and MnO. Calcination was conducted at 900 °C for 2 h and sintering at 1335 °C for 1 h. The secondary maximum in permeability (SMP) of uncalcined ferrites was shifted to higher temperature and does not clearly appear in the initial permeability against temperature plot. The values of initial permeability of the uncalcined ferrites increase rapidly with increasing temperature up to 100 °C, then either increased gently or levelled off. In the working temperature range, 80 to 100 °C, the values of all the ferrites, regardless of the degree of calcination were well above 2000. Above 80 °C, the uncalcined and one-third calcined ferrites had the lowest and the second lowest loss factor values ( $< 3 \times 10^{-6}$ ), respectively. A dense and homogeneous structure of smaller grains with small pores was prevalent in the uncalcined and one-third calcined ferrites.

## 1. Introduction

In a review Das [1] concluded that calcination can produce a low loss ferrite, whereas the ferrite prepared from the uncalcined oxide mixture shows higher permeability and higher loss. Alam *et al.* [2] reported that calcination is important for higher permeability and lower losses. Apparently, the effect of calcination on the quality of Mn–Zn ferrites is controversial.

According to Kimura and Ohiba's findings [3] that  $\approx 50$  wt%  $\alpha$   $Fe_2O_3$  in the Mn–Zn ferrite reacts with MnO and ZnO to form spinels at 900 °C. It seems that there is no need to add all the  $Fe_2O_3$  required for the formation of Mn–Zn ferrites to the mix for one calcination since 50 wt%  $Fe_2O_3$  remains unreacted, which results in a considerable processing cost increase. The remaining  $\approx 50$  wt%  $Fe_2O_3$  could be added to the mix after calcination. The purpose of the present work was to investigate the effect of partial or non-calcination on the quality of Mn–Zn ferrites.

## 2. Experimental procedure

### 2.1. Materials

Raw materials such as iron oxide, zinc oxide and manganite ( $\gamma$ - $MnOOH$ ) to produce manganese oxide for the preparation of Mn–Zn ferrites are industrial grade. The chemical composition of iron oxide and manganite is listed in Tables I and II. The zinc oxide is of 99.43% purity.

### 2.2. Procedure

The amount of the oxides and oxide hydrate required

for the preparation of the Mn–Zn ferrite specimens in the present work was calculated in accordance with chemical formulae,  $Mn_{0.764} Zn_{0.187} Fe_{2.049} O_4$  and  $Mn_{0.687} Zn_{0.272} O_4$ . A powder mix in deionized water with a small amount of alcohol ( $\approx 1$  wt% water added) as a dispersant was ground in an attrition mill for 2 h in accordance with the weight ratio powders:

TABLE I Chemical compositions of iron oxide

Constituent	Content (wt %)
$Fe_2O_3$	99.3
MnO	0.27
$SiO_2$	0.016
CaO	0.016
$Cl^-$	0.067
$H_2O$	0.10
Ig loss	0.17

Note: Average particle size 0.85  $\mu m$

TABLE II Chemical composition of manganite

Constituent	Content (wt %)
Mn	62.54
$MnO_2$	69.20
$SiO_2$	0.01
CaO	0.005
MgO	0.209
$H_2O$	0.35

Note: Needle shape particle, size 0.85  $\mu m$

deionized water: ball = 1:1:4. The steel balls were 6.35 mm in diameter. The attrition mill was of 400 cm<sup>3</sup> and 300 r.p.m.

Calcination was conducted at 900 °C for 2 h in an electric furnace. The calcined mixes were removed from the furnace after normal furnace cooling to room temperature. They were then crushed in a vibration mill and ground in an attrition mill for 4 h to which additives were added. The average size of the ground mixes was 1 μm, which was determined by a commercial sub sieve sizer. The calcined or uncalcined or both powders were mixed in an attrition mill for 2 h to achieve homogeneity for a mix (Table III).

Powders of Mn-Zn ferrite compositions, either calcined or uncalcined, were manually mixed with water containing 2 wt % PVA of 15 ml per 100 g powders prior to forming. Pellets were obtained by having powders passed through - 0.3 + 0.1 mm opening screens.

Specimens were pressed in the form of toroids of 30 mm OD, 22 mm ID and 4 mm thickness under a load of 150 MPa. Prior to pressing, dies were lubricated with calcium stearate.

The specimens were heated in an electric furnace with atmosphere control. The heating rate was

10 °C min<sup>-1</sup> up to 1000 °C and 6 °C min<sup>-1</sup> above 1000 °C. The specimens were kept at 1335 or 1345 °C for 1 h in the air. The specimens were then cooled at a rate of 4 °C min<sup>-1</sup>. Prior to 1100 °C during the cooling, the oxygen content inside the furnace must be lowered rapidly to 0.05 wt % by introduction of nitrogen.

Measurements were carried out on wound toroids. A magnetic hysteresis loop tracer and magnetic intensity of 10 Oe and full flux density of 10000 G were employed. A toroid was wound with 50 turns of primary winding and 10 turns of secondary winding. A HP4274 multifrequency LCR meter was used to measure values of inductance and *Q*. Values of initial permeability were computed from those of inductance.

### 3. Results and discussion

As can be seen from Tables IV and V, the third-calcinated ferrites meet the commercial ferrite specification for use in flyback transformers and switching power supply cores while the full-calcinated ferrites meets or fails to meet the commercial specification. Moreover, the third-calcinated ferrites have lower loss factor values in general. Apparently, partial-calcinated

TABLE III Degree of calcination for various types of Mn-Zn ferrites

Type	Degree of calcination	Remark
F41 F51	Third-calcined	The calcined mix consisting of total amount of ZnO and third amount of Fe <sub>2</sub> O <sub>3</sub> + MnO required for the formation of Mn-Zn ferrites and the sintered mix consisting of the previously calcined mix and the remaining two thirds amount of Fe <sub>2</sub> O <sub>3</sub> + MnO.
F44 F54	Half-calcined	The calcined mix consisting of total amount of ZnO and half amount of Fe <sub>2</sub> O <sub>3</sub> + MnO required and the sintered mix consisting of the previously calcined mix and the remaining half amount of Fe <sub>2</sub> O <sub>3</sub> + MnO.
F42 F52	Full-calcined	The mix consisting of the required amount of oxides calcined.
F43	Uncalcined	Calcination process was omitted.

Note: The sintering aid consisting of 0.05 wt % CaO + 0.05 wt % SnO<sub>2</sub> + 0.05 wt % V<sub>2</sub>O<sub>5</sub> was added before mixing.

TABLE IV Magnetic properties of Mn<sub>0.764</sub> Zn<sub>0.187</sub> Fe<sub>2.049</sub> O<sub>4</sub> ferrites

Type	B <sub>r</sub> (G)	H <sub>c</sub> (Oe)	B <sub>s</sub> (G)	μ <sub>i</sub> 20 kHz 25 °C	tan δ/μ <sub>i</sub> 20 kHz 25 °C
F42 (Full-calcined)	1318	0.111	5244	1600	5.8 × 10 <sup>-6</sup>
F44 (Half-calcined)	1368	0.135	5230	1900	4.7 × 10 <sup>-6</sup>
F41 (Third-calcined)	1322	0.138	5228	2125	3.6 × 10 <sup>-6</sup>
F43 (Uncalcined)	1384	0.199	5008	1700	3.8 × 10 <sup>-6</sup>

TABLE V Magnetic properties of Mn<sub>0.687</sub> Zn<sub>0.272</sub> Fe<sub>2.041</sub> O<sub>4</sub> ferrites

Type	B <sub>r</sub> (G)	H <sub>c</sub> (Oe)	B <sub>s</sub> (G)	μ <sub>i</sub> 20 kHz 25 °C	tan δ/μ <sub>i</sub> 20 kHz 25 °C
F52 (Full-calcined)	1183	0.135	5278	2500	3.9 × 10 <sup>-6</sup>
F54 (Half-calcined)	1037	0.130	5270	2900	2.5 × 10 <sup>-6</sup>
F51 (Third-calcined)	1183	0.157	5068	2600	2.7 × 10 <sup>-6</sup>
F53 (Uncalcined)	942	0.161	4750	2200	3.3 × 10 <sup>-6</sup>

ferrites deserve careful consideration from the point of view of quality and manufacturing cost.

There is a clear peak in an initial permeability against temperature plot for all the ferrites, partially or completely calcined while there is no clear peak at all for the uncalcined ferrites in the same plot. Instead, the values of initial permeability of the uncalcined ferrites increased steadily with increasing temperature until 100 °C then either increased gently or levelled off (Figs 1 and 2). Below 80 °C in general, the values of uncalcined ferrites were lower than those of full-calcined, but above 90 °C the values of uncalcined ferrites were higher than or close to those of full-calcined. In the working temperature range, 80 to 100 °C, the initial permeability values of all the ferrites were above 2000.

As can be seen from Figs 1 and 2, above 80 °C, the uncalcined ferrites have the lowest values of loss factor, and the third-calcined ferrites have the second lowest values; both are lower than or close to commercial products; the values of lost factor for the half-calcined ferrites were either higher than or close to those of full-calcined ferrites. These phenomena suggest the complexity of phase composition development during the formation of ferrites.

It was noticed that in Tables IV and V values of  $H_c$  were all clearly up by the decreasing degree of calcin-

ation. Values of  $B_s$  were lower for the uncalcined ferrites and above 5000 G for the calcined and partial calcined ferrites. In general calcination enhances the value of  $B_s$ . The degree of calcination seems not to significantly affect the values of  $B_r$ . They were  $\approx 1300$  G for  $Mn_{0.764}Zn_{0.187}Fe_{2.049}O_4$  ferrites and 1100 G for  $Mn_{0.687}Zn_{0.272}Fe_{2.041}O_4$  ferrites.

The microstructures corresponding to Figs 1 and 2 are shown in Figs 3 and 4. These micrographs demonstrate that the ferrites of lower loss factor values above 80 °C are characterized by a dense and homogeneous structure consisting of smaller grains in which there are some small pores while the ferrites of higher loss factor values are characterized by a dense but less homogeneous structure consisting of larger grains in which there are some large pores. The lower values of loss factor for the third-calcined and uncalcined ferrites are attributed to the fact that the grain sizes were controlled  $< 10 \mu m$  and more uniform and diffusion and grain growth were retarded by the inhomogeneity of internal structures.

All the ferrites investigated by the present work were added with 0.05 wt % CaO, 0.05 wt % SnO<sub>2</sub> and 0.05 wt % V<sub>2</sub>O<sub>5</sub>. The ferrites without these additives show similar initial permeability values but higher loss factor values. It is believed that these oxide additives form insulating substance in the grain boundary to

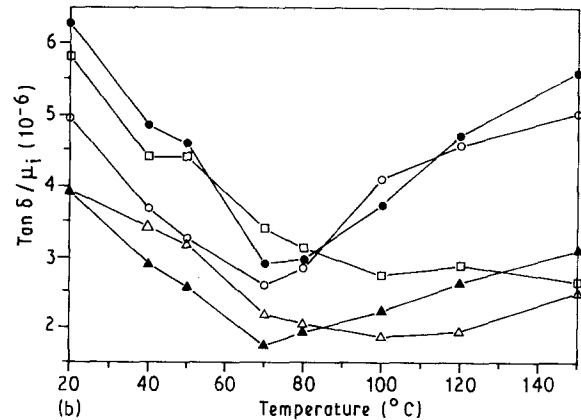
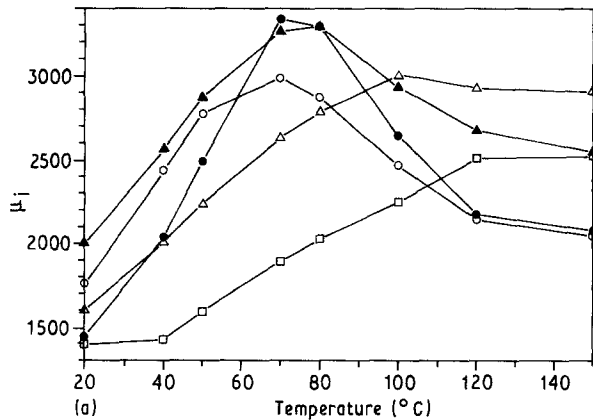


Figure 1 Effect of calcination on initial permeability and loss factor of  $Mn_{0.764}Zn_{0.187}Fe_{2.049}O_4$  ferrites.

(● F42 (full calcined), ○ F44 (half calcined), ▲ F41 (third calcined), △ F43 (uncalcined), □ commercial powders)

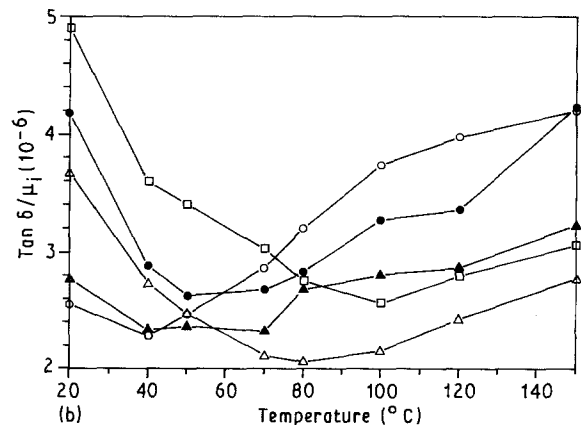
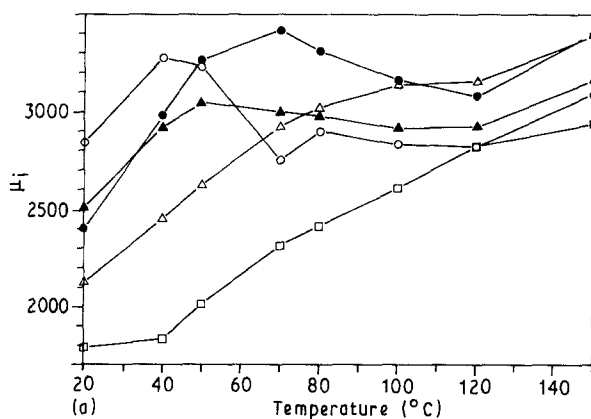


Figure 2 Effect of calcination on initial permeability and loss factor of  $Mn_{0.687}Zn_{0.272}Fe_{2.041}O_4$  ferrites.

(● F52 (full calcined), ○ F54 (half calcined), ▲ F51 (third calcined), △ F53 (uncalcined), □ commercial powders)

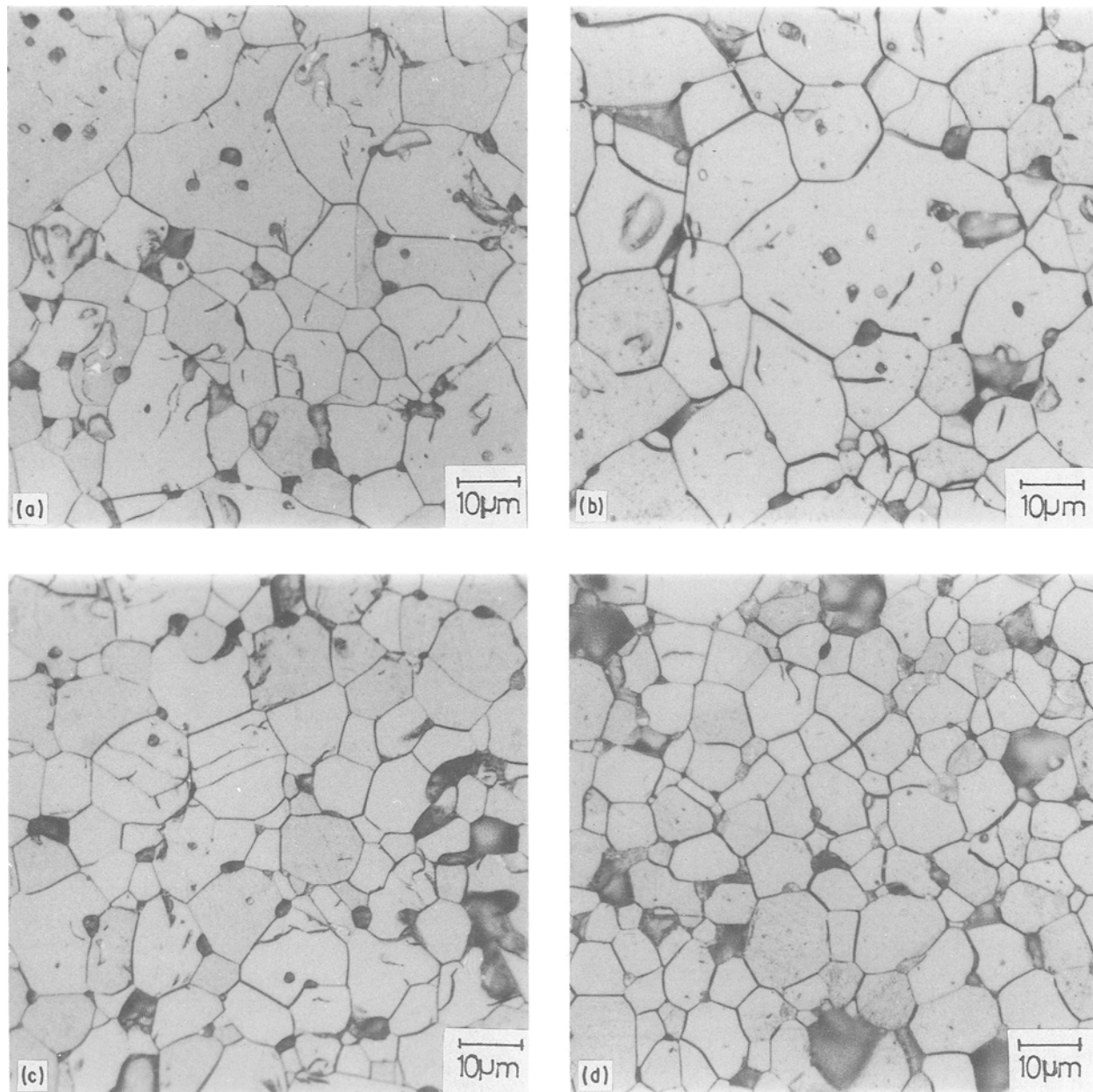


Figure 3 Reflected light micrographs of the  $\text{Mn}_{0.764} \text{Zn}_{0.187} \text{Fe}_{2.049} \text{O}_4$  ferrites with varying degrees of calcination: (a) full-calcined, (b) half-calcined, (c) third-calcined and (d) uncalcined.

increase the resistance and decrease the eddy current in the grain boundary.

Figs 5 to 8 show that the uncalcined ferrites have slightly higher permeability and lower iron loss than the corresponding commercial ferrite products in the frequency range 10 kHz to 1 MHz.

#### 4. Summary

$\text{Mn}_{0.764} \text{Zn}_{0.187} \text{Fe}_{2.049} \text{O}_4$  and  $\text{Mn}_{0.687} \text{Zn}_{0.272} \text{Fe}_{2.041} \text{O}_4$  ferrites containing 0.05 wt % CaO, 0.05 wt %  $\text{SnO}_2$  and 0.05 wt %  $\text{V}_2\text{O}_5$  were prepared by conventional method using manganite ( $\gamma\text{-MnOOH}$ ) as a source of MnO. The partial-calcined ferrites were made by calcining the mix consisting of total amount of ZnO and third or half amount of  $\text{Fe}_2\text{O}_3 + \text{MnO}$  required for the formation of the

Mn-Zn ferrites and sintering the mix consisting of the previously calcined mix and the remaining two thirds or half amount of  $\text{Fe}_2\text{O}_3 + \text{MnO}$ . Calcination was conducted at 900 °C for 2 h and sintering at 1335 °C for 1 h.

There is a clear peak in an initial permeability against temperature plot for all the ferrites, partially or completely calcined while there is no clear peak at all for the uncalcined ferrites. The values of initial permeability of the uncalcined ferrites increased steadily with increasing temperature until 100 °C, then either increased gently or levelled off. In the working temperature range, 80 to 100 °C, the initial permeability values of all the ferrites, partially, completely or uncalcined were well above 2000. Above 80 °C the uncalcined ferrites had the lowest loss factor values and the third-calcined ferrites had the second lowest values ( $< 3 \times 10^{-6}$ ). The ferrites of lower loss factor

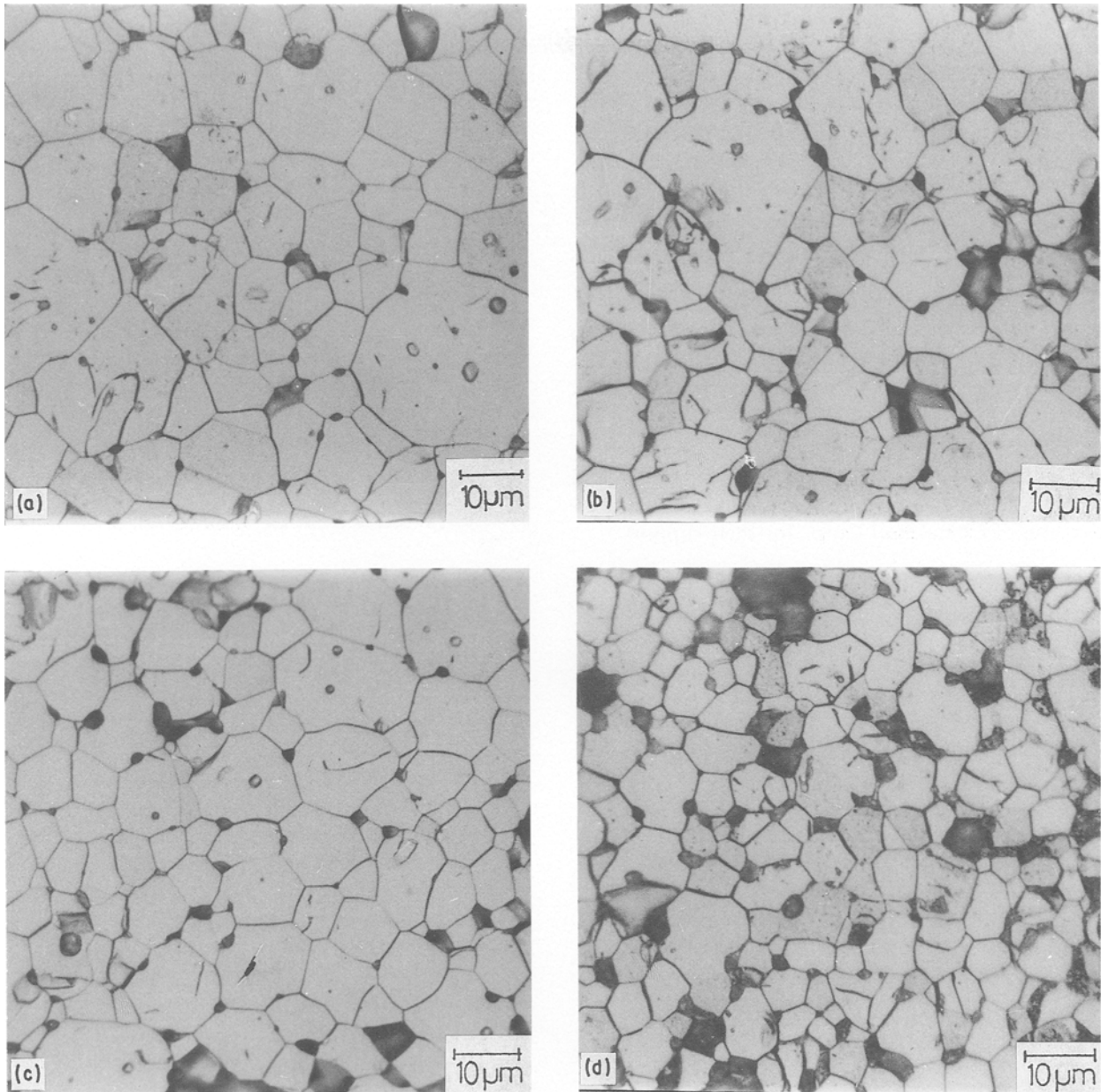


Figure 4 Reflected light micrographs of the  $Mn_{0.687}Zn_{0.272}Fe_{2.041}O_4$  ferrites with varying degrees of calcination: (a) full-calcined, (b) half-calcined, (c) third-calcined, (d) uncalcined.

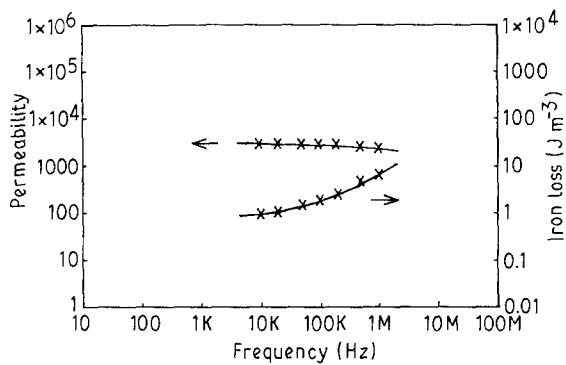


Figure 5 Variation of permeability and iron loss against frequency for the uncalcined  $Mn_{0.764}Zn_{0.187}Fe_{2.049}O_4$  ferrite.

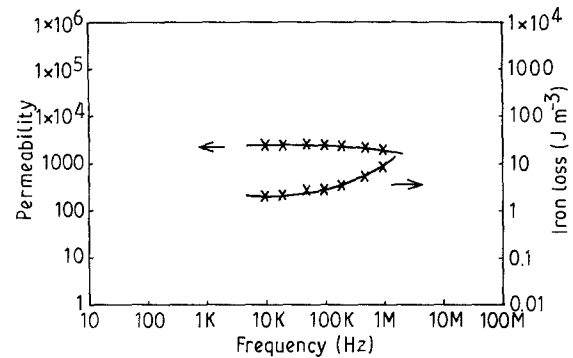


Figure 6 Variation of permeability and iron loss against frequency for the commercial  $Mn_{0.764}Zn_{0.187}Fe_{2.049}O_4$  ferrite.

values above  $80^\circ C$  are characterized by a dense and homogeneous structure consisting of smaller grains with small pores, which was prevalent in uncalcined or third-calcined ferrites while the ferrites of higher loss

factor values are characterized by a dense but less homogeneous structure consisting of larger grains with large pores, which was prevalent in full-calcined or half-calcined ferrites.

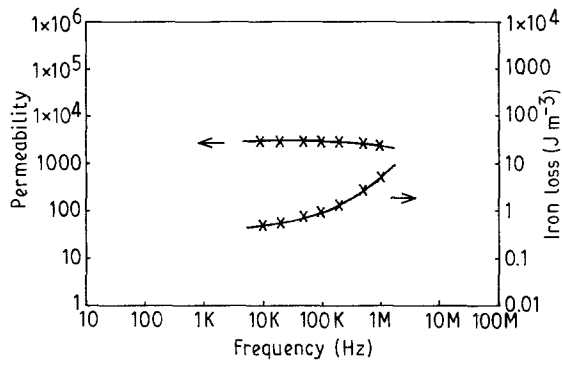


Figure 7 Variation of permeability and iron loss against frequency for the uncalcined  $\text{Mn}_{0.687} \text{Zn}_{0.272} \text{Fe}_{2.041} \text{O}_4$  ferrite.

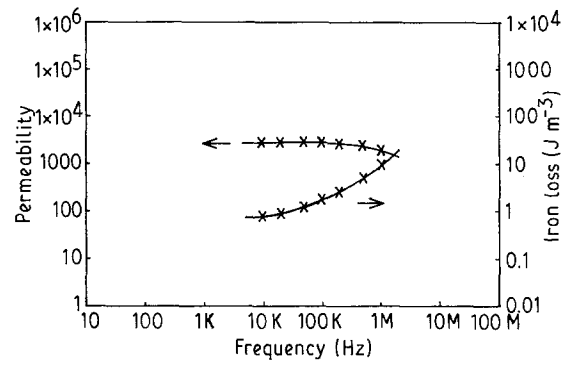


Figure 8 Variation of permeability and iron loss plotted against frequency for the commercial  $\text{Mn}_{0.687} \text{Zn}_{0.272} \text{Fe}_{2.041} \text{O}_4$  ferrite.

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