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Microstructure and Magnetic Properties of \( \text{Ba}_2\text{Cu}_{0.8}\text{Zn}_{1.2}\text{Fe}_{12}\text{O}_{22} \)

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(M.S. Thesis)

September 1988
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MICROSTRUCTURE AND MAGNETIC PROPERTIES OF
\[ \text{Ba}_2\text{Cu}_{0.8}\text{Zn}_{1.2}\text{Fe}_{12}\text{O}_{22} \]

by

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August 1988

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MICROSTRUCTURE AND MAGNETIC PROPERTIES OF

$\text{Ba}_{2}\text{Cu}_{0.8}\text{Zn}_{1.2}\text{Fe}_{12}\text{O}_{22}$

ABSTRACT

The Y-type hexagonal ferrite $\text{Ba}_{2}\text{Cu}_{0.8}\text{Zn}_{1.2}\text{Fe}_{12}\text{O}_{22}$ has been characterized by x-ray diffraction, transmission electron microscopy, analytical electron microscopy, and Lorentz microscopy. Specimens were magnetically oriented so that the c-axes of the hexagonal grains were aligned. The structure was confirmed to have $R3m$ symmetry. The general microstructure consisted of grains about 10 $\mu$m in diameter and 2 $\mu$m in thickness. Intragranular CuZn-ferrite particles were found in some of the grains. The structure of these particles was determined to be diamond cubic with a lattice parameter $\sim 8.4$ Å and the close-packed plane and the close-packed direction parallel to the close-packed plane and the close-packed direction of the matrix phase. The triple grain junctions were found to contain copper-rich and barium-rich intergranular particles, which were believed to be a result of liquid formation during processing. The matrix was found to contain some aluminum contamination and chlorine contamination, which were due to the aluminum crucibles and chloride aqueous solutions used in material processing. The grains contained stacking faults with the fault plane parallel to the basal plane of the grains and with a displacement vector of the type $1/2<0001>$. Attempts to observe domain structure in these ferrites using Lorentz microscopy were not successful. Theoretical
calculation showed that domain formation in thin ferrite specimens was very energetically unfavorable.
MICROSTRUCTURE AND MAGNETIC PROPERTIES OF

$\text{Ba}_2\text{Cu}_{0.8}\text{Zn}_{1.2}\text{Fe}_{12}\text{O}_{22}$

I would like to dedicate this manuscript to my father, a dedicated educator, for sacrificing his freedom to protect the family and for suffering a twelve-and-half year long ordeal in prison.

Thanhtu Huynh
# MICROSTRUCTURE AND MAGNETIC PROPERTIES OF Ba$_2$Cu$_{0.8}$Zn$_{1.2}$Fe$_{12}$O$_{22}$

## TABLE OF CONTENTS

I. Introduction .................................................................................................................. 1  

II. Experiment .................................................................................................................. 5  
   1. Material Processing ................................................................................................. 5  
   2. Specimen Preparation ............................................................................................. 5  
      2.a Phase and Orientation Characterization .......................................................... 5  
      2.b Transmission Electron Microscopy Specimens .............................................. 5  
   3. Experimental Procedures ...................................................................................... 6  

III. Results ..................................................................................................................... 8  
   1. Phase and Orientation Characterization .............................................................. 8  
   2. Microstructural Characterization ......................................................................... 9  
   3. Magnetic Characterization .................................................................................. 13  

IV. Discussion ............................................................................................................... 15  

V. Conclusions ............................................................................................................ 24  

Acknowledgements ...................................................................................................... 25  

References .................................................................................................................. 26  

Table Headings .......................................................................................................... 28  

Figure Captions ......................................................................................................... 29  

Tables .......................................................................................................................... 32  

Figures ......................................................................................................................... 36
I. INTRODUCTION

The application of soft ferrites in recording heads has become significant since the market for magnetic recording tape expanded rapidly in 1968. Jacob estimated that the soft-ferrite market in the USA accounted for some 17 percent of all magnetic materials and could be divided into the groups as shown in Table 1 [1]. The notable advantages of many soft ferrites are their resistivities in the insulating range, attractive magnetic properties at high frequencies and high corrosion resistance [2]. The ferrites commonly used for recording heads are MnZn-ferrites, which have a spinel structure, an initial permeability of the order of 1000 to 2000, and a coercivity of less than 1 Oe [3]. MnZn-ferrites are usable without serious losses up to frequencies of about 500 KHz, although the initial permeability, $\mu_0$, drops rapidly when the operating frequency is above 1 MHz as shown in Figure 1. These ferrites are not suitable for high frequency recording applications, which require that the initial permeability of the soft ferrites remains unchanged over a broad range of frequencies. In general, the head materials for recording at frequencies above 100 MHz should possess properties including high permeability, adequate wear resistance, sufficient hardness to maintain accurate gap geometry, high mechanical strength for the gap to be kept in the prescribed state against rubbing by the video tape, and an adequately reduced level of spurious noise due to such friction [4]. Commercial MnZn-ferrites do not satisfy all of the above conditions when operating at frequencies higher than 100 MHz.
The need for materials used in high frequency recording application led researchers at the Philips laboratory to develop a large class of ferrimagnetic oxides with hexagonal structure [5]. Among these hexagonal ferrites are soft magnetic materials which, like spinel ferrites, are non-metallic in nature and have high resistivity; therefore they can be used at high frequencies. The basic crystallographic and magnetic properties of hexagonal ferrites with M, Y, W, and Z structures have been reviewed by Smit and Wijn [6]. These symbols were chosen for convenience to indicate the four crystal structures $\text{BaFe}_{12}\text{O}_{19}$, $\text{Ba}_2\text{Me}_2\text{Fe}_{12}\text{O}_{22}$, $\text{BaMe}_2\text{Fe}_{16}\text{O}_{27}$, and $\text{Ba}_3\text{Me}_2\text{Fe}_{24}\text{O}_{41}$ respectively, where Me can be any of the transition metal ions. The magnetocrystalline anisotropy of some of these compounds can be such that the spontaneous magnetization lies in the plane perpendicular to the hexagonal c-axis, i.e., (0001). The magnetization can have virtually any direction in this plane, which is called the preferred plane. Although the crystalline, stress, and shape anisotropies may cause a preferred direction of magnetization and oppose rotation within the plane, the effect is usually small [7]. The name “Ferroplana” has been attributed to soft hexagonal ferrites with the above magnetic properties.

The frequency dispersion curves for the permeability $\mu'$ and the loss $\mu''$ are important characteristics of a polycrystalline ferroplana. Both $\mu'$ and $\mu''$ are related to the signal to noise ratio (SNR) of a head noise dominated system as given by the following [8]:

$$\text{SNR} = \sqrt{(\mu'^2 + \mu''^2)/\mu''}$$
A high ratio of $\mu'/\mu''$ will provide an improved signal to noise ratio.

Ferroxplana materials have constant permeabilities for a wide range of frequencies as can be seen in Figure 2, which shows the permeability $\mu'$ and the loss $\mu''$ versus frequency. $\mu'$ stays constant and is larger than $\mu''$ above 100 MHz. A comparison of the frequency dispersion curves of MnZn-ferrite and ferroxplana is shown in Figure 3. At about 3 MHz the ratio $\mu'/\mu''$ of MnZn-ferrite is smaller than 1, and at about 100 MHz it becomes very small. However, $\mu'/\mu''$ of the ferroxplana is still greater than 1 above 100 MHz. Therefore, for high frequency recording applications ferroxplana materials are good candidates.

Among the ferroxplana materials are the Y-type hexagonal ferrites with chemical composition $\text{Ba}_2\text{Me}_2\text{Fe}_{12}\text{O}_{22}$. Figure 4 shows a schematic drawing of the crystal structure of the Y-type ferroxplana, which has the crystal symmetry characterized by the space group $R\bar{3}m$. The length of the c-axis in the smallest elementary cell is 43.5 A and that of the a-axis is 5.8 A [6]. Y-type ferroxplana containing Zn ($\text{Ba}_2\text{Zn}_2\text{Fe}_{12}\text{O}_{22}$ or $\text{Zn}_2\text{-Y}$) has proven to be one of the most suitable hexagonal ferrites for high frequency devices. $\text{Zn}_2\text{-Y}$ has high initial permeability and low magnetic loss associated with high magnetocrystalline anisotropy [9].

In order to control better the planar magnetization of $\text{Zn}_2\text{-Y}$, substitution of zinc ions with other metal ions has been carried out by different groups [9],[10],[11]. However, there has been no detailed study on the relationship between microstructural features and magnetic properties of the substituted $\text{Zn}_2\text{-Y}$. As the performance of magnetic recording heads depends largely on the
magnetic properties of the head materials, control of material processing is crucial. The existence of any second phase particles, precipitates, impurities, or structural defects will certainly affect the magnetic properties of the materials. Therefore detailed characterization of the ferrites is necessary in order to understand the overall performance of the materials.

In this study, the chemical composition of the hexagonal ferrites used is \( \text{Ba}_2\text{Cu}_{0.8}\text{Zn}_{1.2}\text{Fe}_{12}\text{O}_{22} \) or \((\text{Cu},\text{Zn})\text{Y}\). This composition involves partial replacement of Zn ions by Cu ions so as to increase the saturation magnetization, \( M_s \), slightly and the Curie temperature \( T_c \) from \(~100^\circ\text{C}~\) to \(200^\circ\text{C}~[12]\). The materials were polycrystalline with average grain size about 10 \( \mu \text{m} \) in diameter and 2 \( \mu \text{m} \) in thickness and were provided by Kodak-Spin Physics [13]. Specifically, the following points have been investigated:

* Characterization of microstructural defects such as second phase particles, impurities at grain boundaries, and triple grain junctions.

* The microscopic and macroscopic distribution of the chemical composition of the materials.

* Attempts by Lorentz microscopy to observe magnetic domains.

* The effects of microstructural defects on the magnetic properties of the materials.
II. EXPERIMENT

1. MATERIAL PROCESSING:

The ferrooxplana was processed in Eastman Kodak by the coprecipitation method with intended stoichiometric ratios \( \text{BaO:CuO:ZnO:Fe}_2\text{O}_3 = 20:4:7:67 \) weight %. The powders were settled in a rotating magnetic field and oriented in a vibrating sample magnetometer, and isostatically pressed into pellets of 3 mm thick and 18 mm in diameter. The ferrite grains were oriented with their c-axes perpendicular to the broad face of the pellet (Figure 5).

2. SPECIMEN PREPARATION:

2.a Phase and Orientation Characterization:

The bulk samples were mechanically polished for phase and orientation characterization by x-ray diffraction.

2.b Transmission Electron Microscopy Specimens:

Bulk samples of (Cu,Zn)Y were sliced with an Isomet diamond saw to obtain slabs about 600 \( \mu \text{m} \) thick. These slabs were mechanically ground to around 150 \( \mu \text{m} \) and then cut with an ultrasonic drill into 3 mm diameter disk. The disks were dimpled to a thickness of 20 \( \mu \text{m} \) with a dimple grinder then Argon ion-milled to obtain thin areas and carbon-coated for examination by transmission electron microscopy (TEM) and analytical electron microscopy (AEM). Thin foils were prepared with the c-axis both in the plane and perpendicular to the plane of the foils.
3. EXPERIMENTAL PROCEDURES:

Phase and orientation characterization was performed in a Siemens Diffractometer using Cu Kα radiation at a scan rate of 0.025°/sec. X-ray spectra were obtained by radiating the broad face of polished pellets as shown in Figure 5.

Microstructural characterization was carried out in Philips 301 and Philips 400 electron microscopes operated at 100 KV using conventional electron microscopy techniques of bright field and dark field imaging and diffraction. Micro-chemical analysis was performed on the Philips 400 microscope. The chemical composition of the materials was obtained by energy dispersive x-ray (EDX) microanalysis using a beryllium-window detector and a Kevex 8000 Analyst microanalysis system with a nominal electron probe size of 40 nm. Convergent beam electron diffraction (CBED) was performed on the Philips 400 electron microscope to obtain three dimensional structural information of the materials.

Magnetic measurements were performed in a vibrating sample magnetometer by West and Yang [13]. The hysteresis loops were obtained with the field applied in the easy magnetization plane.

In order to observe any magnetic domains and domain walls, and the interaction of domain walls with microstructural features, transmission Lorentz microscopy must be carried out. When the electron beam passes through a magnetized specimen, it is deflected by the field in the specimen. Figure 6 shows the path of electrons going through an uniaxial material with 180° domain walls and its magnetization in the plane of the specimen. Electrons in adjacent 180° domains are deflected in opposite directions.
leading to a deficiency of electrons at A and an excess of electrons at B. In order to observe the domain walls, the objective lens is overfocused (AB) or underfocused (CD) on the specimen. The width of the domain boundary depends on the amount of defocussing [14],[15],[16].

Of course it may be that materials have single domains and hence domain walls may not be visible. Also, it is essential to keep the specimen out of the field of the objective lens to avoid magnetic saturation. Consequently, Lorentz imaging is somewhat qualitative and of relatively low spacial resolution.
III. RESULTS

1. PHASE AND ORIENTATION CHARACTERIZATION:

Figure 7 shows the x-ray spectrum obtained from a magnetically oriented polycrystalline bulk sample of (Cu,Zn)Y. The spectrum was obtained by radiating the broad face of the pellet shown in Figure 5 with Cu Kα radiation. If the grains in the pellet are magnetically oriented with their c-axes pointing in the same direction, only \{0001\} reflections will be present. Figure 7 shows the reflections which are indexed to be the \{0001\} type reflections. A comparison of the x-ray spectra of a (Cu,Zn)Y powder sample, a polycrystalline (Cu,Zn)Y bulk sample, and a single crystal Zn₂Y bulk sample prepared by West and Yang is shown in Figure 8 [13]. The x-ray spectrum of the powder sample reveals all the possible reflections. However, the spectrum of the polycrystalline (Cu,Zn)Y bulk sample is almost identical to that of the single crystal Zn₂Y bulk sample. This shows that only one phase is present in the polycrystalline (Cu,Zn)Y and the ferrite grains are very well oriented. The degree of orientation is illustrated in the hysteresis curve. Figure 9 shows the magnetization hysteresis curves of an unoriented and an oriented polycrystalline (Cu,Zn)Y bulk samples and a single crystalline Zn₂Y bulk sample. The rate of approach to saturation in the oriented polycrystalline sample very much resembles that of the single crystal sample. The squareness ratios, \(M_r/M_s\), of the single crystal sample and the oriented polycrystalline sample are 0.031 ± 0.008 and 0.028 ± 0.008 respectively, where \(M_r\) is the remanent magnetization.
2. MICROSTRUCTURAL CHARACTERIZATION:

The matrix phase contains oriented platelet grains with their \(<0001>\) axes parallel to one another. Figure 10 shows the general microstructure of the \((\text{Cu},\text{Zn})\text{Y}\) matrix phase in two orientations, the c-axes in the plane of the paper and perpendicular to the long axis of the grains (Figure 10a), and the c-axes perpendicular to the plane of the paper (Figure 10b). As can be seen, the grains are oriented. Figure 11 shows typical \([0001]_{ZA}\) CBED and selected area diffraction (SAD) patterns and bright field (BF) and dark field (DF) micrographs. The CBED pattern in Figure 11a reveals three-fold symmetry, which agrees with the \(R\bar{3}m\) symmetry of \(Y\)-type ferroxplana reported in the literature [5],[17]. The residual contrast in the BF and DF micrographs is due to ion thinning during specimen preparation. Figure 12 shows an EDX spectrum of the grain in Figure 11. Microanalysis of this and other such spectra shows that the barium oxide, copper oxide, zinc oxide, and iron oxide concentrations are in the correct proportion compared to the starting oxides. The average values of the oxide weight % of ten matrix grains are shown in Table 2; these values agree with the stoichiometric composition of the starting materials.

Intragranular particles have been observed in these ferrites. The \(<111>\) direction of these particles is parallel to the \(<0001>\) direction of the matrix. Figure 13 shows the \([111]_{ZA}\) CBED and SAD patterns, BF and DF micrographs of an intragranular particle. The particle exhibits well defined facets and trace analysis has shown that particles have the following orientation relationship with the matrix:
\[ (111)_p \parallel (0001)_m \]
\[ \langle 220 \rangle_p \parallel \langle 11\bar{2}0 \rangle_m \]

Figure 14 shows the EDX spectrum of the intragranular particle, in which no barium peak is observed. Microanalysis shows that this particle is CuZn-ferrite as can be seen from Table 3 which lists its chemical composition. The structure of the particle has been determined using CBED, a technique which gives three dimensional crystallographic information [18]. The point group and space group of the particle have been deduced by tilting it to different zone axes and obtaining the CBED patterns. Figure 15 shows CBED patterns of major zones which have the overall symmetry of a cubic system. The \([011]_Z\) shows a two-fold symmetry and is characteristic of either a FCC or a diamond cubic structure. If it is FCC, the \{200\} reflections should be visible, but if it is diamond cubic, very weak or no \{200\} reflections are allowed. However in thick crystals, due to dynamical conditions, the \{200\} reflections will be seen due to double diffraction [13],[18]. The \([001]_Z \) CBED pattern in Figure 15 shows no \{200\} reflection, but in the \([011]_Z \) they are present due to double diffraction of \((1\bar{1}1) + (11\bar{1}) = (200)\). Further evidence is shown in the \([012]_Z \) and \([013]_Z \) CBED patterns. The \{200\} reflections are invisible in the \([012]_Z\), but they are present in the \([013]_Z\) due to double diffraction of \((1\bar{3}1) + (13\bar{1}) = (200)\). Thus, from the above analysis, the structure of the Ba-deficient particle has been determined to be diamond cubic.

Figure 16 shows a similar particle in the \([100]_Z \). The lattice parameter of the particle can be obtained from the CBED pattern (Figure 16a) by measuring the spacing from the center disk to the
first order Laue zone [19]. The spacing has been measured to be 27.2 mm. With the camera length calibrated to be 290 mm, the lattice parameter is calculated to be 8.4 Å.

Some of the triple grain junctions (TGJ) contain intergranular particles which, by x-ray microanalysis, show high concentrations of either copper or barium. Figures 17a and 17b show the microdiffraction pattern and BF image of an intergranular particle with a high concentration of copper. The EDX spectrum of the particle is shown in Figure 18, from which chemical analysis indicates that approximately 94 at% of copper and 5 at% of iron are present as shown in Table 4.

Figures 19a and 19b show the microdiffraction pattern and BF image of a barium-rich intergranular particle. Figure 20 shows the EDX spectrum of the particle, from which chemical analysis indicates that approximately 60 at% of barium, 30 at% of silicon, and 7 at% of iron are present as shown in Table 5.

In addition to the above observation, aluminum contamination has been observed. Its presence is possible due to the aluminum crucibles used for processing the materials. Figure 21 shows the SAD and BF micrographs of an aluminum-contaminated region. As marked in the BF micrograph, this region consists of small grains of aluminum. The EDX spectrum of the same area is shown in Figure 22. As can be seen in the spectrum, a large aluminum peak and a small iron peak are present. Table 6 shows the chemical composition of this region with approximately 95 at% of aluminum and 4 at% of iron.

The synthesis of (Cu,Zn)Y involves metal chloride aqueous
solutions and it is possible to find chlorine-rich regions in the matrix as shown in Figure 23. The EDX spectrum of this chlorine-rich region is shown in Figure 24. Table 7 gives the chemical analysis of this region, which consists of approximately 19 at% of chlorine.

The matrix phase is not always defect free, and in particular, stacking faults have been observed. The bright field images of the stacking faults consist of a series of alternate dark and white fringes parallel to the line of intersection of the foil surface and the plane of the faults, and are symmetrical about the center as shown in Figure 25. However, due to anomalous absorption the dark field images of the fringes are asymmetrical, and depending on the value of $\alpha = 2\pi g \cdot R_F$, where $\alpha$ is a phase factor introduced into the transmitted and diffracted beams due to the faulted region of a crystal, $g$ is the operating reflection, and $R_F$ is the displacement vector, the fringe contrast is similar to that of the bright field images at one edge and complementary at the other. Thus the symmetry properties of fault contrast are sensitive to the value of $\alpha$. In FCC and hexagonal closed packed (HCP) crystals, simple faults are characterized by $\alpha = \pm 2\pi/3$ and have the symmetry properties described above. However, more complex situations may occur in HCP structures. In the present analyses the symmetry properties are similar to those known for $\alpha = \pm 2\pi/3$, hence from visibility contrast experiments it is possible to evaluate $R$ since $g$ is indexed from the diffraction pattern. Fringes are visible for $\alpha \leq \pm 2\pi/3$ and invisible for $\alpha = n2\pi$ where $n$ is an integer [14],[15]. Figures 25b, c, d and e show the BF and DF images of the stacking faults in a ferrite
grain with \( g = 2ar{1}11 \) and \( g = 0ar{1}11 \) in an orientation \([1ar{2}13]_A\). As the dark field images of the stacking faults have been taken with opposite \( g \), fringe contrast reversal occurs at the top of the foil. The faults are invisible imaged with \( g = \bar{1}010 \) as shown in Figures 25f and 25g, and with \( g = 000\bar{6} \) in the \([1210]_A\) shown in Figure 26.

The displacement vector \( \mathbf{R}_F \) has been determined using defect contrast analysis [14] as shown in Table 8, which shows the values of \( g \cdot \mathbf{R}_F \) for different \( g \) and \( \mathbf{R}_F \). Two types of displacement vector are possible, \( 1/2<0001> \), generated by the condensation of a layer of vacancies or interstitials in a close-packed hexagonal crystal, and \( 1/6<20\bar{2}3> = 1/2[0001] + 1/3<10\bar{1}0> \), generated by a similar condensation followed by a Shockley shear partial [20]. For the displacement vector \( \mathbf{R}_F \) of the type \( 1/2<0001> \) (Table 8), the faults are visible imaged with \( g = 2\bar{1}11 \) and \( g = 0\bar{1}11 \), and are invisible imaged with \( g = \bar{1}010 \) and \( g = 000\bar{6} \). This analysis agrees with the observation of the stacking faults shown in Figures 25 and 26. Thus the displacement vector is deduced to be of the type \( 1/2<0001> \).

More experiments and especially high resolution lattice fringe imaging are needed to completely characterize and understand these faults since the \( 1/2<0001> \) displacement corresponds to a missing layer of cations or anions but without violating neighboring charges.

3. MAGNETIC CHARACTERIZATION:

Specimens with the c-axis both in the plane and perpendicular to the plane of the specimen have been prepared for magnetic characterization by Lorentz imaging. However, no domain structure
has ever been observed. Verweel reports a domain size of 10 μm with domain walls parallel to the basal plane in single crystalline Zn₂-Y [21], which have similar magnetic properties as magnetically oriented polycrystalline (Cu,Zn)Y. It is possible that in (Cu,Zn)Y either the domain size is very large or only single domains exist as will be discussed in the following section.
IV. DISCUSSION

The x-ray diffraction data of the magnetically oriented polycrystalline (Cu,Zn)Y show a high degree of orientation and agree with the measured magnetic properties of the materials as shown in Figure 9. This figure compares the hysteresis curves of a single crystal, an oriented and a non-oriented polycrystalline ferroplana. Both the single crystal and oriented crystalline samples approach saturation in a similar way. However, the saturation magnetization for the oriented polycrystalline materials is higher than that for the single crystals due to partial replacement of Zn ions by Cu ions in the starting materials (approximately 38.7 emu/g for oriented polycrystalline materials and 35.5 emu/g for single crystals). Both hysteresis curves have the same characteristics such as small coercivity (approximately 6 Oe), high saturation magnetization. The ability to achieve highly oriented grains and to increase the $T_c$ makes the polycrystalline material an attractive candidate for high frequency recording heads.

The formation of the barium-deficient intragranular particles is possibly due to phase separation during processing. Although the materials have been washed with either water or HCl during processing [13], these particles appear to be unaffected. Owing to the small quantity of these particles, they were not detected in either x-ray diffraction or scanning electron microscopy [13]. The orientation relationship between the particles and the matrix has been found to be:

$$\{111\}_p \parallel \{0001\}_m$$

$$\langle 220 \rangle_p \parallel \langle 11\bar{2}0 \rangle_m$$
There was no noticeable strain induced by the structural mismatch at the interfaces of the matrix and the particles as shown in Figures 13 and 16. In order to obtain further evidence of this, the spacings of the close-packed planes of the particles and of the matrix have been determined. The plane spacing, $d_{220}$, of the particles has been calculated to be around 2.96 Å, and the plane spacing, $d_{1120}$, of the matrix phase has been found to be 2.94 Å. These values agree quite well within experimental errors. Thus the interface is expected to be very coherent with no strain field as in fact is observed.

X-ray microanalysis has revealed the intragranular particles to be CuZn-ferrite, although statistically few of them have been observed. Their intrinsic magnetic properties may be quite different from those of the matrix phase, and they may be detrimental to the magnetic performance of the materials. However, from the comparison of the hysteresis curves in Figure 9, the materials appear to behave much as the single crystalline materials. No further information of the effects of these particles on the magnetic performance of the materials is available at this point due to difficulties in observing magnetic domain structure in the electron microscope.

The intergranular phase at the triple grain junctions which are either copper-rich or barium-rich is a result of liquid phase sintering and is expected to have undesirable effects on the magnetic properties of the materials. In order to eliminate this intergranular phase it is necessary to study the phase equilibrium between individual oxides. However, except for the
equilibrium phase diagram for BaO and Fe$_2$O$_3$, there are no available phase diagrams for the other binary systems.

The microstructural characterization results indicate possible directions that might be taken to avoid the formation of intragranular particles as well as the intergranular particles. The crystallographic relations and facetting of the intragranular particles are consistent with their forming in the solid state, possibly by phase separation. Undoubtedly the intergranular phase is a result of liquid formation during processing.

Attempts to observe domain structures in (Cu,Zn)Y by Lorentz microscopy have not been successful. It was assumed that the stray fields (magnetic fields created by the electromagnetic lenses) in the microscope are strong enough to saturate the specimen as the specimen sits between the objective pole pieces. However, Lorentz microscopy experiments have been performed with the objective lenses turned off so that the magnetic field created by the objective lenses is near zero. The stray fields created by other electromagnetic lenses are insignificant to saturate the specimen.

Owing to the stray field assumption being inappropriate, the investigation has been turned to examine the feasibility of domain formation in the thin specimens used in the Lorentz microscopy experiment. Calculations have been carried out first using an isolated grain model to obtain the order of magnitude for the critical size $L_c$ of a single-domain grain, the magnetostatic energies for a single-domain grain and a multi-domain grain, and the equilibrium domain size for the multi-domain grain. Then a correction is made to these calculations to obtain the values of the
above parameters for an aligned polycrystalline model.

The critical size $L_c$ of single-domain particles is defined as the particle size below which the particles prefer to remain in the single-domain state because they will have the lower energy as can be seen in Figure 27. $L_c$ can be calculated from the following expression [3]:

$$L_c = \frac{1.7 \varphi}{\pi^2 M_s^2}$$

(1)

where $\varphi$ is the domain wall energy and $M_s$ is the saturation magnetization. $M_s$ can be obtained from the hysteresis curve, as shown in Figure 9. With the density of the materials being 5.45 g/cm$^3$, $M_s$ is determined to be:

$$4\pi M_s = 37 \text{ emu/g} = 37 \text{ emu/g} \times 5.45 \text{ g/cm}^3 = 201.65 \text{ emu/cm}^3$$

Therefore $M_s = 16.05 \text{ emu/cm}^3$.

The domain wall energy can be obtained from the following expression:

$$\varphi = [(0.3k_B T_c \pi^2 K_a)/a_0]^{1/2}$$

(2)

where $k_B$ is the Boltzmann constant, $T_c$ is the Curie temperature (437 K), $K_a$ is the anisotropy constant ($\sim 10^6$ ergs/cm$^3$), and $a_0$ is the lattice parameter (5.8 Å). Upon substituting these values into Eq.(2), $\varphi$ is found to be 1.81 ergs/cm$^3$.

With $\varphi$ being 1.81 ergs/cm$^3$ and $M_s$ being 16.05 emu/cm$^3$, $L_c$ can be determined:

$$L_c = \frac{1.7 \varphi}{\pi^2 M_s^2} = \frac{1.7 \times 1.81 \text{ ergs/cm}^3}{\pi^2(16.05 \text{ emu/cm}^3)^2}$$

$L_c = 9.64 \times 10^{-5} \text{ cm} = 1 \mu m$
This is a small value compared to the grain size of the materials. The average grain size is approximately 10 μm. However, it must be noted that the value of $L_c$ is obtained by assuming that the grains are isolated from one another, thus giving only the lower limit to the critical grain size. This means that in an oriented polycrystalline sample $L_c$ can be larger due to the interaction across grain boundaries and the lower demagnetizing field.

In order to find out whether the single-domain grain or the multi-domain grain is favorable, calculation and comparison of the total energies of the two cases have been carried out by assuming the shape of the grains to be flat disks with a radius of 5 μm and a thickness of 1000 Å (Figure 28).

The total magnetic energy of a specimen consists of four terms:

$$E_{tot} = E_a + E_\lambda + E_s + E_w$$

where $a$, $\lambda$, $s$, and $w$ stand for anisotropy, magnetostrictive, magnetostatic and wall, respectively. Minimizing the various terms under the existing conditions such as the composition, shape, size and crystal orientation of the specimen leads to a minimum total energy which corresponds to a stable structure [2].

Consider the grain with single domain in Figure 28a. This grain has zero $E_a$ and zero $E_w$. Its $E_\lambda$ is approximately zero because the single domain can adjust to magnetostriction without causing internal stress [2]. The only non-zero term is $E_s$. Shape anisotropy of a specimen must be considered when calculating the magnetostatic energy of the specimen. In order to simplify the problem, assume the flat disks in Figure 28 to be oblate spheroids as shown in Figure 29. Magnetization of an oblate spheroid is
difficult along the short y axis and easy along any axis normal to y, i.e., in the plane of the disk. The magnetostatic energy of the single-domain grain is:

\[ E_s = \frac{1}{2}M_s^2N_x \]  

(3)

where \( N_x \) is the demagnetizing coefficient along x. For the ratio \( x/y \) being 100, \( N_x \) is \( 4\pi(7.76 \times 10^{-3}) \). \( E_s \) is then determined to be:

\[ E_s = \frac{1}{2}(16.05 \text{ emu/cm}^3)^2 4\pi(7.76 \times 10^{-3}) = 157.78 \text{ ergs/cm}^3 \]

Then the magnetostatic energy per unit area is:

\[ E = E_sL \quad \text{where } L \text{ is the diameter of the disk in Figure 28a.} \]

The total energy of the single-domain grain is:

\[ E_{\text{tot}} = E = E_sL = 157.78 \text{ ergs/cm}^3 \times 10^{-3} \text{ cm} = 0.16 \text{ ergs/cm}^2 \]

Now consider the total energy of the same grain with multiple domains. The magnetostatic energy per unit area of the multi-domain grain is given by [3]:

\[ E_s = 1.7M_s^2D \]  

(4)

where \( D \) is the thickness of the slab-like domains as shown in Figure 28b. The total energy is the sum of the magnetostatic and wall energies:

\[ E_{\text{tot}} = E_s + E_w \]

\[ E_{\text{tot}} = 1.7M_s^2D + \varphi L/D \]  

(5)

The minimum energy occurs at:

\[ \frac{dE_{\text{tot}}}{dD} = 1.7M_s^2 - \frac{\varphi L}{D^2} = 0 \]

\[ D = \left[ \frac{\varphi L}{(1.7M_s^2)} \right]^{1/2} \]  

(6)

Substitute Eq.(6) in Eq.(5) and obtain \( E_{\text{tot}} \):  

\[ E_{\text{tot}} = 2(1.7M_s^2\varphi L)^{1/2} \]
The equilibrium domain size can be calculated from Eq. (6):

\[ D = \left[ \frac{\phi L}{1.7 M_s^2} \right]^{1/2} \]

\[ = \frac{(1.81 \text{ ergs/cm}^2)(10^{-3} \text{ cm})}{[1.7(16.05 \text{ emu/cm}^3)^2]}^{1/2} \]

\[ = 5.73 \times 10^{-4} \text{ cm} \]

\[ = 6 \mu\text{m} \]

These results are also obtained for an isolated grain. The results for a polycrystalline specimen are expected to be different. If a grain is surrounded by several grains, there will be interaction across the grain boundaries, and the demagnetizing field tends to decrease due to easy nucleation at grain boundaries. The saturation magnetization of a poly-uniaxial crystal has been calculated to be about \((1/2)^{1/2}\) times that of the separated crystallites [22]. Thus the magnetostatic energy is about one-half that of the separated crystallites, the domain size of the polycrystal is about \(\sqrt{2}\) times larger than the separated crystallites, and the total domain energy is \((1/2)^{1/2}\) times that of the separated crystallites.

With these correction factors, the magnetostatic energy of a polycrystalline specimen with single domain is about 0.08 ergs/cm\(^2\). The magnetostatic energy of a polycrystalline specimen with multiple domains is 1.57 ergs/cm\(^2\), and the wall energy is about 2.23 ergs/cm\(^2\). Then the total energy of the polycrystalline specimen is the sum of the magnetostatic energy and the wall energy. It is calculated to be 3.81 ergs/cm\(^2\). The equilibrium domain size is then approximately 10 \(\mu\text{m}\).

The ratio of total energies of the polycrystalline specimen
before and after division into domains is:

\[
\frac{E_{\text{tot}}(\text{multi-domain})}{E_{\text{tot}}(\text{single-domain})} = \frac{3.81}{0.08} = 47.63
\]

A 48-fold increase in energy has been obtained by the creation of domains. Therefore domain formation is not favorable. Further evidence to support this conclusion can be obtained from the equilibrium domain size, which is comparable to the grain size for the geometry considered in the above calculation, i.e., thin foil approximation. It is possible that although the thin foil has domains, the domain walls lie along the grain boundaries, and the contrast of the grain boundaries overwhelms the contrast of the domain walls.

It must be emphasized that the above calculation only gives the order of magnitude to the critical grain size, the magnetostatic energies, and the equilibrium domain size in thin foils, and it provides a qualitative explanation as to why domain walls cannot be observed in the electron microscope. These values may not be valid for the bulk materials. In a thin foil the magnetization vectors are very likely confined to the plane of the foil [23], this means that the preferred directions on which the magnetization vectors tend to lie in the thin foil may not be the same as the easy axes of the bulk materials. Therefore domain formation may be possible in bulk materials even though it is not favorable in thin foils.

In summary, it should be pointed out that much work remains to be done on these materials in terms of an improved method of
material processing to obtain single phase (Cu,Zn)Y. A thorough study on the phase equilibrium of the oxides would be helpful to eliminate the intragranular and the intergranular particles, which are believed to have detrimental effect to the magnetic properties of the materials. The Bitter powder technique can be used to observe magnetic domain structure in the bulk samples, however, it may not be possible to resolve the interaction between the microstructural features and the domain walls. There is no doubt that the magnetically oriented polycrystalline (Cu,Zn)Y will be an attractive candidate for high frequency recording applications once a better understanding of the material processing is obtained.
V. CONCLUSIONS

The high degree of grain orientation in the magnetically oriented polycrystalline (Cu,Zn)Y allows the materials to have the saturation magnetization and magnetocrystalline anisotropy similar to those of single crystalline Zn$_2$Y. The microstructure of the polycrystalline ferrites consists of large grains about 10 μm in diameter and 2 μm in thickness. The matrix grains contain some intragranular particles which are Ba-deficient and have a diamond cubic structure with a lattice parameter of 8.4 Å. The orientation relationship between the intragranular particles and the matrix phase is such that the close-packed plane of the particles is parallel to the close-packed plane of the matrix phase, and the close-packed direction of the particles is parallel to the close-packed direction of the matrix phase. This implies that the particles precipitate from the matrix. Some of the triple grain junctions of the matrix phase contain copper-rich and barium-rich particles. The observed aluminum contamination and chlorine contamination in the matrix phase are most likely caused by the crucibles and chloride aqueous solutions used in material processing. The matrix phase contains stacking faults. The fault plane is parallel to the basal plane and the displacement vector is of the type $1/2<0001>$. The magnetostatic energy of a thin polycrystalline specimen with a single domain is calculated to be lower than that of the same specimen with multiple domains. This is believed to be the cause for not being able to observe domains in the thin specimen with the electron microscope.
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REFERENCES


TABLE HEADINGS

Table 1: Market value of U.S. production of soft ferrites in 1968 [1].
Table 2: Average chemical composition of the oxide weight percentage obtained from ten matrix grains.
Table 3: Chemical composition of the intragranular particle.
Table 4: Chemical composition of the Cu-rich triple grain junction.
Table 5: Chemical composition of the Ba-rich triple grain junction.
Table 6: Chemical composition of the Al-contaminated region.
Table 7: Chemical composition of the Cl-contaminated region.
Table 8: Values of $g \cdot R_F$ for various $g$ and $R_F$ for faults in (Cu,Zn)Y.
FIGURE CAPTIONS

Figure 1  Variation of initial permeability $\mu_0$ with frequency for MnZn-ferrite [3].

Figure 2  Frequency dispersion curve of ferroxplana [13].

Figure 3  Comparison of the frequency dispersion curves of MnZn-ferrite and ferroxplana [13].

Figure 4  Cross-section of the Y-type hexagonal ferrite unit cell. The arrows indicate the spin orientations, and the crosses indicate centers of symmetry. [6].

Figure 5  Schematic drawing of a magnetically oriented polycrystalline (Cu,Zn)Y bulk sample.

Figure 6  Observation of magnetic domains by out-of-focus method. Electrons are deviated in opposite directions in adjacent 180 degree domains, leading to a deficiency of electrons at A and an excess at B. The contrast of the virtual images at C and D is reversed [15].

Figure 7  X-ray spectrum of a magnetically oriented polycrystalline (Cu,Zn)Y bulk sample.

Figure 8  Comparison of the x-ray spectra of (a) a bulk sample of Zn$_2$-Y, (b) a bulk sample and (c) a powder sample of (Cu,Zn)Y [13].

Figure 9  Hysteresis curves of an unoriented and an oriented polycrystalline (Cu,Zn)Y bulk samples, and a single crystalline Zn$_2$-Y bulk sample [13].

Figure 10  Transmission electron micrographs of (Cu,Zn)Y matrix phase with c-axis (a) in the plane and (b) perpendicular
to the plane of the paper.

Figure 11  (a) $[0001]_{ZA}$ CBED pattern of a matrix grain.  
(b) $[0001]_{ZA}$ SAD pattern of the same grain.  (c) Bright field image with $g = 2\overline{1}10$.  (d) Corresponding Dark field image.

Figure 12  EDX spectrum of a normal grain.

Figure 13  (a) $[111]_{ZA}$ CBED pattern from an intragranular particle, 
(b) Conventional SAD pattern, (c) Bright field image with $g = 0\overline{2}2$, (d) Corresponding dark field image.

Figure 14  EDX spectrum of the intragranular particle.

Figure 15  CBED patterns mapping the stereographic triangle of an intragranular particle illustrating its diamond cubic structure.

Figure 16  (a) $[100]_{ZA}$ CBED pattern from an intragranular particle, 
(b) Conventional SAD pattern, (c) Bright field image with $g = 00\overline{4}$, (d) Corresponding dark field image.

Figure 17  (a) Microdiffraction and (b) Bright field image of an intergranular particle with high concentration of Cu.

Figure 18  EDX spectrum of the Cu-rich intergranular particle.

Figure 19  (a) Microdiffraction and (b) Bright field image of an intergranular particle with high concentration of Ba.

Figure 20  EDX spectrum of the Ba-rich intergranular particle.

Figure 21  (a) SAD and (b) Bright field of an Al-contaminated region.

Figure 22  EDX spectrum of the Al-contaminated region.

Figure 23  (a) SAD, (b) Bright field, (c) Dirty dark field of a Cl-contaminated region.
Figure 24  EDX spectrum of the Cl-contaminated region.

Figure 25  (a) Conventional SAD pattern in $[1\bar{2}1\bar{3}]_ZA$, (b) Bright field image of the stacking faults imaged with $\mathbf{g} = 2\bar{1}1\bar{1}$, (c) Corresponding centered dark field image with opposite $\mathbf{g}$, (d) Bright field image of the stacking faults imaged with $\mathbf{g} = 0\bar{1}1\bar{1}$, (e) Corresponding centered dark field image with opposite $\mathbf{g}$, (f) Bright field image of the stacking faults imaged with $\mathbf{g} = \bar{1}0\bar{1}0$, (g) Corresponding centered dark field image with opposite $\mathbf{g}$.

Figure 26  (a) Conventional SAD pattern in $[1\bar{2}1\bar{0}]_ZA$, (b) Bright field image of the stacking faults imaged with $\mathbf{g} = 000\bar{6}$, (c) Corresponding centered dark field image with opposite $\mathbf{g}$.

Figure 27  A schematic drawing illustrating the relation between the energy $E$ of a crystal and its linear dimensions $L$ for two kinds of magnetic state $[3]$.

Figure 28  Geometry for magnetostatic energy calculation for (a) a single-domain grain and (b) a multi-domain grain.

Figure 29  Geometry of an oblate spheroid.
Table 1. Market Value of U.S. Product of Soft Ferrites in 1968.

<table>
<thead>
<tr>
<th>Application</th>
<th>Millions of dollars</th>
<th>Percent of market</th>
</tr>
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<tbody>
<tr>
<td>Computer memory cores</td>
<td>$ 55</td>
<td>50</td>
</tr>
<tr>
<td>Television receivers</td>
<td>20</td>
<td>18</td>
</tr>
<tr>
<td>Communications and radio components, recording heads,</td>
<td>20</td>
<td>18</td>
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<tr>
<td>magnetostriction transducers</td>
<td></td>
<td></td>
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<tr>
<td>Telephone communications</td>
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<td>11</td>
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<tr>
<td>Microwave ferrite components</td>
<td>3</td>
<td>3</td>
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<tr>
<td><strong>Total</strong></td>
<td><strong>110</strong></td>
<td><strong>100</strong></td>
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Table 2

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<th>Normal Grain</th>
<th>% Fe$_2$O$_3$</th>
<th>% CuO</th>
<th>% ZnO</th>
<th>% BaO</th>
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<tr>
<td>Average</td>
<td>65.05 ± 0.96</td>
<td>5.99 ± 0.29</td>
<td>7.44 ± 0.35</td>
<td>21.52 ± 0.63</td>
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Table 3

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<th>Intergranular particle</th>
<th>Fe</th>
<th>Cu</th>
<th>Zn</th>
<th>Ba</th>
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<td>Atomic %</td>
<td>65.37 ± 0.51</td>
<td>13.99 ± 0.26</td>
<td>19.18 ± 0.34</td>
<td>0.72 ± 0.17</td>
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Table 4

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<tr>
<th>Cu TGJ</th>
<th>Fe</th>
<th>Cu</th>
<th>Zn</th>
<th>Ba</th>
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<tbody>
<tr>
<td>Atomic %</td>
<td>4.84 ± 0.16</td>
<td>93.68 ± 0.74</td>
<td>0.69 ± 0.12</td>
<td>0.79 ± 0.21</td>
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### Table 5

<table>
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<tr>
<th>Ba TGJ</th>
<th>Fe</th>
<th>Cu</th>
<th>Zn</th>
<th>Ba</th>
<th>Si</th>
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<td>Atomic %</td>
<td>7.37 ± 0.36</td>
<td>2.63 ± 0.35</td>
<td>0.63 ± 0.26</td>
<td>59.74 ± 1.54</td>
<td>29.63 ± 0.40</td>
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### Table 6

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<tr>
<th>Al Contamination</th>
<th>Fe</th>
<th>Cu</th>
<th>Zn</th>
<th>Ba</th>
<th>Al</th>
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<tr>
<td>Atomic %</td>
<td>3.28 ± 0.30</td>
<td>1.07 ± 0.20</td>
<td>0.36 ± 0.16</td>
<td>0.62 ± 0.34</td>
<td>94.67 ± 1.14</td>
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### Table 7

<table>
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<th>Cl Contamination</th>
<th>Fe</th>
<th>Cu</th>
<th>Zn</th>
<th>Ba</th>
<th>Cl</th>
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<tr>
<td>Atomic %</td>
<td>46.76 ± 0.67</td>
<td>21.63 ± 0.53</td>
<td>4.01 ± 0.27</td>
<td>8.67 ± 0.57</td>
<td>18.92 ± 0.28</td>
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## Table 8

<table>
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<th>$R_F$</th>
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<th>1010</th>
<th>0006</th>
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<td>1/2</td>
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<tr>
<td>$1/6&lt;2023&gt;$</td>
<td>3/2</td>
<td>1/6</td>
<td>-2/3</td>
<td>-3</td>
</tr>
</tbody>
</table>
Figure 1
Figure 2
Figure 3
Figure 4

\[ Y = \text{Ba}_2\text{Me}^{II}_2\text{Fe}_{12}\text{O}_{22} \]

- 4 $\leftrightarrow$ +2 $\leftrightarrow$
- 4 $\leftrightarrow$ +2 $\leftrightarrow$ +2 $\leftrightarrow$
- 8 $\leftrightarrow$ +2 $\leftrightarrow$ +4 $\leftrightarrow$

- O
- Ba
- Fe$^{III}$/Me$^{II}$

C: 43.5 Å

a: 5.8 Å

XBL 888-2702
Figure 5

$\text{Ba}_2\text{Cu}_0.8\text{Zn}_{1.2}\text{Fe}_{12}\text{O}_{22}$

XBL 888-2701
Figure 6
Figure 8
Figure 9

- Single Crystal
- Oriented Poly Crystal
- Unoriented Poly Crystal

emu/g vs. Applied Field (Oe)
Figure 12
Figure 13
Ba-DEFICIENT PARTICLE
(DIAMOND CUBIC)

Figure 15
Figure 17

XBB 887-7046
Figure 19
Figure 20
Figure 22
Figure 23
Figure 25
(cont.)
a: Single-domain crystal
b: Multi-domain crystal

Figure 27
Figure 28
Figure 29