Synthesis of copper and lithium copper ferrites as high magnetization materials

K.E. Kuehn, D. Sriram, S.S. Bayya, J.J. Simmins, and R.L. Snyder New York State College of Ceramics at Alfred University, Alfred, New York 14802

(Received 26 April 2000; accepted 2 May 2000)

The ferrite with composition $Cu_{0.5}Fe_{2.5}O_4$ was heat treated in air and in reducing atmospheres to different temperatures within the solid solution region confirmed by dynamic high-temperature x-ray characterization. The samples were quenched in oil and air, and lattice parameter, Curie temperature, and saturation magnetization measurements were completed. The magnetization measurements for these samples showed a maximum $4\pi M_{\rm s}$ of 0.7729 and 0.5426 T at 10 and 300 K, respectively. The cationic distribution based on the low-temperature $4\pi M_s$ measurements is $(Cu^{+}_{0.24}Fe^{3+}_{0.76})_{A}[Cu^{+}_{0.26}Fe^{3+}_{1.74}]_{B}O_{4} \rightarrow 4.9 \ \mu_{B}. \ X\text{-ray-pure} \ Cu_{0.5}Fe_{2.5}O_{4} \ \text{samples}$ were also synthesized by slow cooling from the formation temperature to 900 °C in a reducing atmosphere. A temperature- P_{O_2} diagram for the stability of Cu_{0.5}Fe_{2.5}O₄ under the conditions of the experiment was determined. Low-temperature $4\pi M_s$ measurements did not indicate an increase in the Cu⁺ A site occupancy for the samples cooled to 900 °C in a reducing environment above those samples that were quenched from high temperature. Curie temperatures for all Cu_{0.5}Fe_{2.5}O₄ samples ranged from 348 to 369 °C. Lithium additions (0.1 mol/unit formula) to copper ferrite $Li_{0.1}Cu_{0.4}Fe_{2.5}O_4$ decreased the room-temperature $4\pi M_s$ values to 0.5234 T with a corresponding decrease in the 10 K measurements to 0.7047 T. From the low-temperature magnetization measurements, the distribution was $(Cu^{+}_{0.15}Fe^{3+}_{0.85})_{A}[Cu^{+}_{0.25}Li^{+}_{0.1}Fe^{3+}_{1.65}]_{B}O_{4} \rightarrow 4.48 \ \mu_{B}.$

I. INTRODUCTION

Investigations of a wide variety of spinel ferrite compositions have taken place in the past few decades with the goal of determining the composition, which would increase the saturation magnetization of the ferrite crystal structure. The benefits in obtaining a higher saturation magnetization in the cubic spinel ferrits are well known, the most exciting being the possible increase in microwave communication frequencies further into the gigahertz range. However, there has been no reported success in obtaining usable saturation magnetizations in excess of the 0.55 T found in zinccontaining ferrites.

The problem with existing ferrites containing zinc is the spin-canting phenomenon, observed for high concentrations of Zn^{2+} . The zinc ion has a tetrahedral site preference within the spinel structure and therefore weakens or dilutes the tetrahedral sublattice moment. This causes an initial increase in the net moment; however, for higher Zn concentrations the magnetic coupling between the octahedral and tetrahedral lattice weakens causing a rapid decrease in the net magnetization due to spin–lattice canting. This was illustrated by Gorter.¹ Dionne² postulated that the most favorable spinel compositions capable of exceeding existing saturation magnetizations are the generic monovalent cation ferrites. A monovalent cation with tetrahedral site preference would allow dilution of the tetrahedral site moment while keeping a significant tetrahedral site Fe^{3+} concentration to maintain the magnetic coupling between the two sublattices. Theoretically, this would allow 2 mol of Fe^{3+} on the octahedral sublattice while maintaining the coupling with a partial dilution of the tetrahedral sublattice moment.

The monovalent copper ferrite system is one case for a monovalent cation with tetrahedral site preference. The composition $Cu_{0.5}Fe_{2.5}O_4$, where the copper is monovalent and occupies the tetrahedral site, should ideally exhibit a net magnetic moment of 7.5 μ_B at 0 K. However, the site distribution of the copper ions over the available sites in the spinel is complicated by the multivalent nature of the copper ion. Studies involving the $CuFe_{2.5}O_4$ system show that the divalent copper cation prefers the octahedral site almost exclusively.^{3,4} In addition, the synthesis of the ideal $Cu_{0.5}Fe_{2.5}O_4$ ferrite is further complicated by the desire of the Fe³⁺ cation to oxidize any nearby octahedral Cu^{+, 5} The studies of this material have

Downloaded: 25 Mar 2015

1635

^{© 2000} Materials Research Society

caused further disagreement about the distribution and valence state of the copper ion. Previous research involving Cu_{0.5}Fe_{2.5}O₄ has provided lattice parameter values ranging from 8.39 to 8.414 Å.⁶ Likewise, the measured moment has varied from 4.05 to 5.4 μ_B near 0 K.^{6.8}

With the addition of another monovalent cation, such as lithium (which has octahedral site preference), to the system $Cu_{0.5}Fe_{2.5}O_4$, it is thought that the lithium cations will decrease the probability of ferrous ion formation in the spinel structure, thus, increasing the resistivity of the material. The lithium addition will also increase the room-temperature saturation magnetization by reducing the spin-canting phenomena if it is active. Therefore, an optimum between the lithium addition and saturation magnetization can be expected. Calculated magnetic moments per unit formula, assuming ideal placement of the cations, lie in the range 7.5 (pure $Cu_{0.5}Fe_{2.5}O_4$) to 5 (Li_{0.25}Cu_{0.25}Fe_{2.5}O₄) Bohr magnetons at 0 K. The objective of this research is the realization of a ferrimagnet with a room-temperature saturation magnetization in excess of the current practical value of about 0.55 T with sufficiently high resistivity and acceptable dielectric properties for soft ferrite applications.

II. EXPERIMENTAL PROCEDURE

The initial oxides CuO and Fe_2O_3 were rotary calcined at 950 °C in the correct ratio to obtain the final stoichiometry for Cu_{0.5}Fe_{2.5}O₄. The calcination resulted in an initial phase composition CuFe₂O₄ and Fe₂O₃ as determined by x-ray diffraction (XRD). Some properties of the bulk starting powder are shown in Table I.

The stability region for Fe₂O₃ was determined via dynamic x-ray analysis.⁷ With a locally automated Philips diffractometer equipped with a scanning position sensitive detector (PSD) and iron radiation ($K_{\alpha_{1,2}} \lambda = 1.938$ Å; $K_{\beta_1} \lambda = 1.757$ Å) it is possible to observe the formation of the Cu_{0.5}Fe_{2.5}O₄ spinel structure at elevated temperatures. The sample is mounted onto a platinum strip, which is heated electrically under computer control. The low- and high-temperature phase boundaries, in air, as determined by this *in situ* method, are 1200 and 1350 °C, respectively. These values are in good agreement with those found in the literature.^{8,9}

The instability of the $Cu_{0.5}Fe_{2.5}O_4$ compound was noted previously.⁹ To maintain a single-phase material from high temperature in air it is necessary to quench the

TABLE I. Starting powder informati	Starting powder informatio	wder informati	powder	Starting	TABLE I.
------------------------------------	----------------------------	----------------	--------	----------	----------

Ferrite	Mean size (µm)	Standard deviation (µm)	Specific surface area (m ² /g)	Density (g/cm ³)
Cu _{0.5} Fe _{2.5} O ₄	2.51	1.26	4.93	5.37
Li _{0.1} Cu _{0.4} Fe _{2.5} O ₄	2.03	1.15	5.05	5.13

material from the desired temperature rapidly enough to prevent the decomposition to $CuFe_2O_4$ and Fe_2O_3 . The dynamic x-ray system was also used to determine more precisely the quench rate needed to "lock-in" singlephase $Cu_{0.5}Fe_{2.5}O_4$ ferrite. Since the thermal mass of the stage and sample is very small, controlled quenches of up to 20 °C/s are possible. The two-phase material was heated to 1250 °C and checked for completeness of reaction. It was then quenched at different rates to determine the minimum rate needed to maintain the $Cu_{0.5}Fe_{2.5}O_4$ ferrite phase purity. The minimum quench rate needed was determined to be 7 °C/s in air. Note that this was for a powder film roughly 1–3 microns thick.

The temperature stability of $Cu_{0.5}Fe_{2.5}O_4$ was also determined for the purpose of synthesizing bulk samples. With the dynamic XRD unit the precursor composition was heated into the phase-pure region and verified as to its phase purity. The sample was quenched on the hotstage and then reheated to temperatures up to 500 °C. Continuous scanning of the diffraction pattern while holding the sample at the temperature in question allowed the time for decomposition into Fe_2O_3 and a cubic copper containing ferrite to be determined. The time– temperature decomposition plot is shown as Fig. 1.

Sample preparation and measurement

The two-phase Fe_2O_3 and $CuFe_2O_4$ powder was isostatically pressed into rods at 103 MPa (15,000 psi). The rods were sintered according to a sintering curve to near full density. The final rod was wafered with a diamond wafering blade into 0.4×1.5 cm disks. The disks were then heated in a tube furnace in flowing air or air-CO₂ (for reduced P_{O_2} atmospheres) to temperatures within the solid solution region, as determined by the hot-stage xray data, and quenched into oil. Accurate lattice param-



FIG. 1. Time for decomposition of $Cu_{0.5}Fe_{2.5}O_4$ into Fe_2O_3 and copper ferrite at a given temperature as determined by dynamic x-ray characterization.

JOURNALS

1636

eters were determined for each of the samples. The lattice parameters were determined by the zero background holder external standard method.¹⁰

The sample diffraction peak locations were determined by profile fitting the sample peaks with a split Pearson VII profile¹¹ and correcting the *d*-value with an external standard calibration curve. The lattice parameter was then calculated on the basis of a least-squares refinement of the *d*-values. The lattice parameter for the $Cu_{0.5}Fe_{2.5}O_4$ heated in air, versus the quench temperature, is tabulated in Table II.

Saturation magnetization measurements were performed on the superconducting quantum interference device (SQUID) at the State University of New York at Buffalo. SQUID measurements were taken at 10 and 300 K on powdered samples quenched from different temperatures and on the phase-pure samples from the related oxygen pressures and temperatures in the Cu_{0.5}Fe_{2.5}O₄ and Li_{0.1}Cu_{0.4}Fe_{2.5}O₄ systems. Part of the hysteresis curve, for different samples of the $Cu_{0.5}Fe_{2.5}O_4$ phase, used for calculating the saturation magnetization data, is shown in Fig. 2. Curie temperature measurements were performed by Trans-Tech, Inc., Adamstown, MD, and are tabulated in Table III. Bulk samples for saturation magnetization measurements were also produced. The samples were quenched in air to reduce the possibility of thermal shock. Samples on both sides of the transition temperature including the twophase samples above and below the solid solution region were prepared. XRD of the samples was carried out in order to verify the phase purity of the material. The phase stability region of Cu_{0.5}Fe_{2.5}O₄ was traced as a function of temperature and oxygen partial pressure (P_{Ω_2}) . The partial pressure of oxygen in the tube furnace was controlled with a CO₂ air mixture. A zirconia sensor (oxygen sensor model OX manufactured by AACC/Zircoa, Solon, OH) positioned adjacent to the sample was used to monitor the $P_{\Omega_{i}}$. Following heat treatment in air within the solid solution region the samples were subject to a 5 $^{\circ}C/$ min furnace cool with simultaneous decrease in oxygen pressure. When the designated P_{O_2} and final temperature were reached, the samples were quenched in oil. The

TABLE II. Lattice parameter for $Cu_{0.5}Fe_{2.5}O_4$ heated in air mixture followed by oil quenching.

composition of the sample was determined by XRD. An example of the experimental temperature and P_{O_2} profiles is shown as Fig. 3. The final temperature and oxygen partial pressures, including phase compositions, for all samples involved in the reduced P_{O_2} study are shown in Fig. 4. These curves show how the P_{O_2} needs to be changed during cooling as a function of temperature to stabilize the Cu_{0.5}Fe_{2.5}O₄ phase for the conditions of the study.

To characterize the valence of the iron cations, Mössbauer studies were performed on the samples quenched, into oil, from the $Cu_{0.5}Fe_{2.5}O_4$ stability region in air. Resistivity measurements were also made on quenched samples, crushed and dry pressed into pellets. In order to maintain consistency in testing of different samples, all of the powder samples were dry pressed into pellets under identical conditions. This meant that in making each of the pellets the same amount of powder was weighed out and the uniaxial pressing pressures used were exactly the same (51 MPa or 7500 psi). All pellets obtained had the same dimensions (1.7-cm diameter and 10 mm thick). The opposite faces of each of the pellets (cross section) were electroded with silver paste. Resistivity



FIG. 2. SQUID magnetization measurements at 10 K for $Cu_{0.5}Fe_{2.5}O_4$ samples quenched from various temperatures.

TABLE III. Curie temperature measurements for air $Cu_{0.5}Fe_{2.5}O_4$ samples cooled at 20 °C/min from peak temperature.

Temperature (°C)	Lattice parameter (Å)	Standard deviation σ (Å)
1226	8.4154	0.0003
1246	8.4152	0.0002
1286	8.4162	0.0004
1326	8.4187	0.0007
1348	8.4189	0.0007
1366	8.4200	0.0005
1372	8.4191	0.0004
1404	8.4184	0.0006

Final temperature (°C)	Lattice parameter (Å)	Standard deviation σ (Å)	Figure of merit (7)	Curie temperature (°C)
1326	8.4181	0.0007	137	350
1348	8.4185	0.0005	142	369
1366	8.4192	0.0007	131	364
1372	8.4167	0.0004	251	348
1246	8.4152	0.0002	354	353
1226	8.4162	0.0003	319	356

http://journals.cambridge.org

data for the samples was obtained using an ac impedance analyzer (RF impedence analyzer, model 4191A, Hewlett Packard, Palo Alto, CA). The conductance of the pellet sample was obtained at three different frequencies: 0.1, 1, and 10 kHz. From these data, the average conductivity was then extracted and the resistivity values calculated.

The full width at half-maximum (FWHM) of the outermost peak of the Mössbauer spectra and the resistivity measurements obtained for samples from different quench temperatures are tabulated in Table IV. Figure 5 shows a sample of the Mössbauer data obtained for



FIG. 3. Example of $Cu_{0.5}Fe_{2.5}O_4$ samples temperature–oxygen partial pressure processing path.



 $Cu_{0.5}Fe_{2.5}O_4$. A clear drop in the FWHM of the outer Mössbauer peak and increase in the resistivity of the samples at higher temperature were observed.

III. RESULTS AND DISCUSSION

The results of the lattice parameter measurements for the final heat treatment in air followed by oil quenching are tabulated in Table II and shown in Fig. 6.

TABLE IV. FWHM of the outermost Mössbauer peak and resistivity for $Cu_{0.5}Fe_{2.5}O_4$ heated in air mixture followed by oil quenching.

Temperature (°C)	FWHM (mm/s)	Resistivity (ohm/cm)
1226	1.108	5.08
1246	1.082	5.28
1286	0.985	5.59
1326	0.906	8.78
1348	0.804	11.93



FIG. 5. Mössbauer data for $Cu_{0.5}Fe_{2.5}O_4$ in air at Alfred University.



FIG. 4. Final temperatures and oxygen partial pressures for $Cu_{0.5}Fe_{2.5}O_4$ samples showing a region of stability (pure-phase region) for the conditions of the experiment. The horizontal line represents the partial oxygen pressure of air.

FIG. 6. Lattice parameter versus final heat-treatment temperature for oil-quenched $Cu_{0.5}Fe_{2.5}O_4$.

http://journals.cambridge.org

Three sigma error bars are shown indicating a 99.87% confidence level, and Fig. 6 shows that there is a significant difference in the lattice parameter of the material depending on the temperature from which the sample was quenched. The trend toward larger lattice parameter at high temperature may be explained by the increase in the formation of Cu⁺, which migrates to the preferred tetrahedral position. Qualitatively, Cu⁺ has a larger ionic radius than the Cu²⁺ ion and Cu⁺ prefers the smaller four-coordinated site in the spinel structure. Therefore, the expansion is intuitively explainable by the increase in Cu⁺ on the tetrahedral sites which displaces the smaller Fe^{3+} cation to the octahedral sublattice resulting in an overall expansion of the lattice. The lattice then begins to contract as the copper is lost from the ferrite lattice in the form of CuFeO₂.

The lattice parameter of the bulk air-quenched samples was determined in the same manner as the oil-quenched samples. The results of the $4\pi M_s$ at room temperature and density measurements are tabulated in Table V. The $4\pi M_s$ values given have been scaled to the theoretical density of 5.25 g/cm³. The samples heated at 1360 °C and the furnace-cooled samples are not phase pure but were scaled for comparison. The 3σ error bars in all cases are larger than for the oil quench samples; this indicates that there is a gradient in lattice parameter through the sample thickness. Since the outer surface of the samples cools more rapidly than the interior, it is suspected that this outer surface is composed of the larger lattice parameter material. Unfortunately the "skin" of the samples is removed when the sample is ground into a sphere for $4\pi M_s$ measurements so that the results of the measurements may not be indicative of the lattice parameters measured. Figure 7 illustrates the mean airquenched sample lattice parameters indicated by the horizontal line and the corresponding $4\pi M_s$ measurements relative to the lattice parameter measurements of the oil-quenched samples.

The SQUID magnetization measurement on the samples quenched into oil, from the air mixture, seen from Table VI, shows an increasing trend as the temperature of the quench is increased. The lattice parameter results along with the Mössbauer and resistivity studies

TABLE V. Bulk samples lattice parameter and magnetization as determined for $Cu_{0.5}Fe_{2.5}O_4$ heated in air/CO₂ mixture followed by air quenching.

Temperature (°C)	Lattice parameter (Å)	Standard deviation σ (Å)	Density (%) theoretical	Corrected $4\pi M_{\rm s}$ (T)
(1) 1265	8.4160	0.0024	94	0.4948
(2) 1350	8.4182	0.0012	92	0.5173
(3) 1360	8.4197	0.0012	93	0.5070
furnace cool	8.4111	0.0009	96	0.3539



FIG. 7. Air-quenched bulk samples lattice parameters relative to oilquenched samples including $4\pi M_s$ measurements. The mean lattice parameter is indicated by a horizontal line with corresponding $4\pi M_s$.

for the quenched samples seem to confirm the SQUID magnetization results showing a mixture of both Fe^{2+} and Fe^{3+} , hence the redox of Cu (and Fe), at low temperatures, and the formation of pure or close to pure monovalent but disordered $Cu_{0.5}Fe_{2.5}O_4$ phase at higher temperatures.

The maximum value of $4\pi M_s$ determined from the SQUID measurements for Cu_{0.5}Fe_{2.5}O₄ was found to be 0.7729 and 0.5426 T at 10 and 300 K, respectively, for the sample quenched into oil from a temperature of 1348 °C and P_{O_2} of 0.21 atm. The cation distribution based on the low-temperature 0.7729 T $4\pi M_s$ measurement, in light of the Mössbauer, lattice parameter, and resistivity data is

$$(Cu^{+}_{0.24}Fe^{3+}_{0.76})_{A}[Cu^{+}_{0.26}Fe^{3+}_{1.74}]_{B}O_{4} \rightarrow 4.9 \ \mu_{B}$$

However, the presence of small amounts of Cu^{2+} in the sample cannot be completely ruled out. Consistent with small amounts of Cu^{2+} that may be present, the spinel structure can be written as

$$\begin{array}{c}(Cu^{+}_{0.24}Fe^{3+}_{0.76})_{A}[(Cu^{+}_{0.26-x}Cu^{2+}_{x})(Fe^{3+}_{1.76-x}Fe^{2+}_{x})]_{B}O_{4}\\ \rightarrow 4.9\ \mu_{B}\quad.\end{array}$$

The corresponding cation distribution in the case of $\text{Li}_{0.1}\text{Cu}_{0.4}\text{Fe}_{2.5}\text{O}_4$ based on the maximum value of $4\pi M_{\rm s}$ of 0.7047 T (4.48 $\mu_{\rm B}$) is

$$\begin{array}{c} (Cu^{+}_{0.15}Fe^{3+}_{0.85})_{A}[(Cu^{+}_{0.25}Li^{+}_{0.1}Fe^{3+}_{1.65}]_{B}O_{4} \\ \rightarrow 4.48 \ \mu_{B} \quad . \end{array}$$

The lattice parameter and magnetization of the $Cu_{0.5}Fe_{2.5}O_4$ and $Li_{0.1}Cu_{0.4}Fe_{2.5}O_4$ phases are tabulated in Table VII. A decrease in magnetization value on the addition of Li suggests that the low values of saturation

J. Mater. Res., Vol. 15, No. 7, Jul 2000

Final temperature	Final	Lattice parameter	Standard deviation σ	Figure of merit	
(°C)	P_{O_2}	(Å)	(Å)	(7)	$4\pi M_{\rm s}$ (T)
Cu _{0.5} Fe _{2.5} O ₄					
1226	0.21	8.4162	0.0003	319	0.7474
1286	0.21	8.4164	0.0004	251	0.7640
1326	0.21	8.4181	0.0007	137	0.7718
1366	0.21	8.4192	0.0007	131	0.7569
1348	0.21	8.4185	0.0005	66	0.7729
1341	0.17	8.4172	0.0008	91	0.7610
1205	$4.3 imes 10^{-2}$	8.4141	0.0006	145	0.7523
1201	$8.9 imes 10^{-3}$	8.4196	0.0009	103	0.7472
1091	$1.5 imes 10^{-2}$	8.4154	0.0003	268	0.7528
992	$1.2 imes 10^{-2}$	8.4141	0.0004	208	0.7293
889	$2.5 imes 10^{-3}$	8.4162	0.0004	146	0.7648
789	$1.4 imes 10^{-3}$	8.4158	0.0002	397	0.6733
Li _{0.1} Cu _{0.4} Fe _{2.5} O ₄ Samples					
1226	0.21	8.4000	0.0009	69	0.7047
1323	0.21	8.4014	0.0009	77	0.6913
889	$2.5 imes 10^{-3}$	8.3939	0.0009	91	0.6809
789	$1.4 imes 10^{-4}$	8.3957	0.0009	75	0.6618

TABLE VI. SQUID magnetization measurements of powder samples including lattice parameters at 10 K as determined for $Cu_{0.5}Fe_{2.5}O_4$ under conditions similar to those in Figure 3.

TABLE VII. SQUID magnetization measurements of powder samples including lattice parameters at 300 K as determined for $Cu_{0.5}Fe_{2.5}O_4$ and $Li_{0.1}Cu_{0.4}Fe_{2.5}O_4$ under conditions similar to those in Figure 3.

Final temperature	Final P	Lattice parameter $\begin{pmatrix} \lambda \\ \lambda \end{pmatrix}$	Standard deviation $\sigma(\mathring{A})$	Figure of merit	$4\pi M$ (T)
(0)	¹ O ₂	(A)	0 (A)	(7)	$4 m_{s}(1)$
Cu _{0.5} Fe _{2.5} O ₄					
1348	0.21	8.4185	0.0005	66	0.5426
1226	0.21	8.4162	0.0003	319	0.5071
992	$1.2 imes 10^{-2}$	8.4153	0.0002	397	0.4612
$Li_{0.1}Cu_{0.4}Fe_{2.5}O_{4}$					
1226	0.21	8.400	0.0009	69	0.5234

magnetization (from speculated 1.1 T) observed in $Cu_{0.5}Fe_{2.5}O_4$ system is not due to spin–lattice canting but is due to the distribution of Cu^+ on A and B sites.

IV. CONCLUSIONS

The nature of $Cu_{0.5}Fe_{2.5}O_4$ with the presence of multivalent copper and iron ions with differing site preferences makes it a difficult material to study. Ideally, this material is capable of extending the saturation magnetization limit beyond the present day maximum. The expansion of the lattice for high-temperature heat treatments followed by quenching is thought to be due to the redox of Cu^{2+} ion into Cu^+ ion, which in turn migrates to the tetrahedral positions. However, since the temperature at this point is very high, all Cu^+ formed is not able to occupy the preferred tetrahedral site but is disordered between the tetrahedral A-site and octahedral B-site. The key to the ordering of the Cu^+ ions to the tetrahedral A-site, it now seems, is to lower the temperature and at the same time maintain a highly reducing atmosphere to stop redox from occurring. This optimization of temperature and P_{O_2} demands further work on dynamic *in situ* XRD with atmosphere control.

The solid solution region for the composition studied was determined to be from 1200 to 1350 °C. This region was determined via dynamic x-ray characterization. This characterization method was also used to determine that the minimum quench rate necessary to maintain the phase purity of a thin film is 7 °C/s. The rate of decomposition of the $Cu_{0.5}Fe_{2.5}O_4$ structure into Fe_2O_3 and $CuFe_2O_4$ air was also determined.

 $Cu_{0.5}Fe_{2.5}O_4$ may be cooled to temperatures under 1200 °C by decreasing the oxygen partial pressure. In this study, phase-pure $Cu_{0.5}Fe_{2.5}O_4$ ferrite was maintained by slow cooling to 900 °C, 300 °C below the low temperature boundary for this material in air. However, the slow-cooled samples do not show increased saturation magnetization over the samples quenched from the high-temperature formation region. The maximum saturation magnetization for the $Cu_{0.5}Fe_{2.5}O_4$ samples was 0.7729 T at 10 K and 0.5426 T at 300 K. The 300 K saturation magnetization surpasses that of the present zinc-containing ferrite compositions, and due to the mixed nature of the copper distribution over the A and B sites, the composition $Cu_{0.5}Fe_{2.5}O_4$ has great potential to exceed, by far, the present magnetization maximum in the ferrite crystal structure.

REFERENCES

- 1. E.W. Gorter, Philips Res. Rep. 9, 321 (1954).
- 2. G.F. Dionne, J. Appl. Phys. 61, 3865 (1987).
- J. Janicki, J. Pietrzak, A. Porebska, and J. Suwalski, Phys. Status Solidi A 72, 95 (1982).

- 4. X. Tang, A. Manthiram, and J.B. Goodenough, Solid State Chem. **79**, 250 (1989).
- E.Ya. Sapozhnikova, A.G. Davidovich, E.M. Roizenblat, M.A. Zinovik, L.V. Kosheleva, V.M. Maslova, and E.V. Markovskii, Russ. J. Inorg. Chem. (Engl. Transl.) 26, 945 (1980).
- 6. A. Nagarajan and A.H. Agajanian, J. Appl. Phys. 41, 1642 (1969).
- 7. R.L. Snyder and B.J. Chen, Adv. X-ray Anal. 38, 1 (1995).
- 8. S. Miyahara and Y. Yino, Jpn. J. Appl. Phys. 4, 310 (1965).
- M.A. Zinovik and A.G. Davidovich, Russ. J. Inorg. Chem. (Engl. Transl.) 26, 855 (1980).
- S.T. Misture, L. Chatfield, and R.L. Snyder, Powder Diffr. 9, 172 (1994).
- 11. S.A. Howard and R.L. Snyder, J. Appl. Crystallogr. 22, 238 (1989).
- M. Lenglet, J. Kasperek, B. Hannoyer, J. Lopitaux, A. D'Huysser, and J.C. Tellier, J. Solid State Chem. 98, 252 (1992).

