Letters

Structural and lattice parameter changes in the slow cooled and quenched $Cu_xZn_{1-x}Fe_2O_4$ samples

$CuFe_2O_4$ exhibits tetragonal variation [1], changing semiconductive properties [2] and electrical switching [3] when heat-treated under different conditions. In spite of the varied data available on $CuFe_2O_4$ there is a problem in understanding it both in terms of cation distribution and structural changes. It is for this reason that studies on $CuFe_2O_4$ continue to be interesting.

Lattice parameter variation may be intimately associated with cation distribution in the case of copper ferrites. Thus, a mixed ferrite involving Cu^{2+} and another divalent cation with a somewhat predictable behaviour, like Zn^{2+}, can be studied from the point of view of lattice parameter changes with the hope of elucidating the role of copper ion in ferrites.

In the present paper we report our studies on lattice parameter variation with composition and with quenching temperature on the basis of cation distribution.

$Cu_xZn_{1-x}Fe_2O_4$ (where $x = 0$, 0.2, 0.4, 0.6, 0.8 and 1) samples were prepared by a standard ceramic method using AR grade oxides of ZnO, CuO and Fe_2O_3. During this preparation pre-sintering at 700° C for 24 h and powdering of the formed products was followed by final sintering at 950° C and furnace cooling at a rate of 80° C h^{-1}. The completion of the solid-state reaction was confirmed by X-ray diffraction studies carried out on a Philips PM 9920 X-ray diffractometer, using an iron target and 1.937 Å FeK$_\alpha$ radiation. Retaining a set of $Cu_xZn_{1-x}Fe_2O_4$ samples as slow-cooled, the remainder were quenched from 800, 700 and 600° C in air to yield a set of samples for each temperature. For quenching from 800° C, $Cu_xZn_{1-x}Fe_2O_4$ powders were sintered and equilibrated at 950° C for 4 h and furnace cooled to 800° C. After equlibrating for 2 h at 800° C, the powders were suddenly removed from the furnace and air quenched. A similar procedure was adopted for quenching samples from 600 and 700° C.

The Curie temperatures were measured by the techniquè given by Laroia and Sinha [4].

TABLE I Axial ratio variation with quenching temperature for $CuFe_2O_4$

Nature of sample		Axial ratio
Quenched from 800° C	–	1.037
Quenched from 700° C	–	1.039
Quenched from 600° C	–	1.043
Slow cooled from 950° C	–	1.052

From our studies it was observed that samples of $CuFe_2O_4$, furnace cooled from 950° C and air quenched from 800, 700 and 600° C, exhibited a tetragonal structure and the tetragonality varied with the quenching temperature of the samples. In Table I details of the variation of the axial ratio with quenching temperature are given. The variation is shown in Fig. 1. An almost linear relationship is exhibited for the variation of c/a with quenching temperarure; c/a shows maximum value for the sample quenched from 600° C which decreases with an increase in the quenching temperature. The c/a value of the slow-cooled sample is shown in Fig. 1 by "X", indicating that its c/a value is greater than that for the quenched samples. The reported values of the axial ratio for $CuFe_2O_4$ show a variation from 1.03 to 1.06 [5–7]. Our values of c/a given in Table I agree closely with

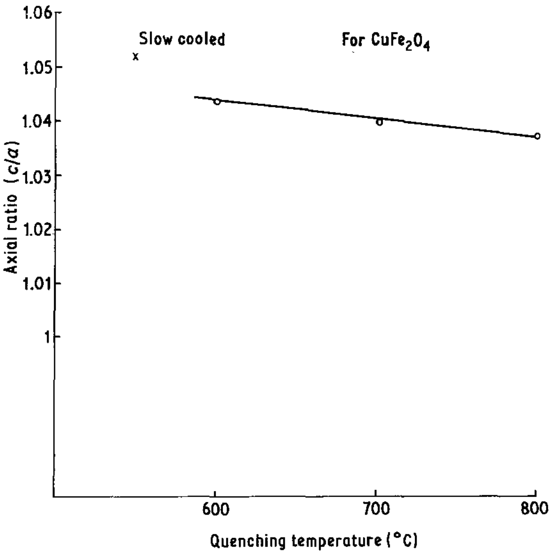

Figure 1 Variation of axial ratio with quenching temperatures for $CuFe_2O_4$.

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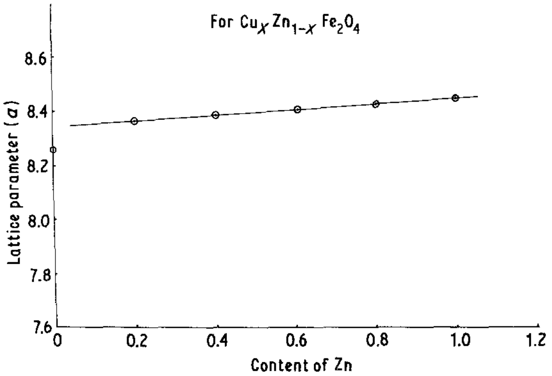

Figure 2 Variation of lattice parameter with content of Zn for $Cu_xZn_{1-x}Fe_2O_4$.

this range of variation for *c/a* values of tetragonal $CuFe_2O_4$.

Our samples of $Cu_xZn_{1-x}Fe_2O_4$ ($x \neq 1$), slow-cooled and quenched from 800, 700 and 600° C showed a cubic structure. In Fig. 2 the variation of lattice parameter a with the Zn content is shown for $Cu_xZn_{1-x}Fe_2O_4$ samples slow cooled from 950° C. It is seen that as the Zn content increases the lattice parameter also increases from that of $CuFe_2O_4$ ($a = 8.256$ Å) to that of $ZnFe_2O_4$ ($a = 8.438$ Å) obeying Vegard's Law. A similar behaviour is observed even in the quenched samples (Fig. 3). The a values for copper ferrite and zinc ferrite show close agreement with the values earlier reported for these ferrites [8, 9]. Fig. 3 shows the variation of a with the quenching temperature for $Cu_xZn_{1-x}Fe_2O_4$ ($x \neq 1$). It is seen that for $Cu_{0.8}Zn_{0.2}Fe_2O_4$ and $Cu_{0.6}Zn_{0.4}Fe_2O_4$ the lattice parameter decreases linearly with an increase in the quenching temperature of the samples. However, the change involved in a in the temperature interval under consideration is smaller for $Cu_{0.6}Zn_{0.4}Fe_2O_4$ than for $Cu_{0.8}Zn_{0.2}Fe_2O_4$. For the remaining samples $Cu_{0.4}Zn_{0.6}Fe_2O_4$, $Cu_{0.2}Zn_{0.8}Fe_2O_4$ and $ZnFe_2O_4$ the lattice parameter a does not show any dependence on the quenching temperature. Table II gives lattice parameter variation with composition and quenching temperature for $Cu_xZn_{1-x}Fe_2O_4$.

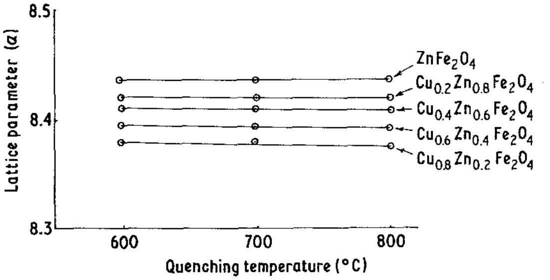

Figure 3 Variation of lattice parameter with quenching temperature for $Cu_xZn_{1-x}Fe_2O_4$.

In Table III cation distribution evaluated from experimental values of Curie temperatures and values of Curie temperatures computed from Gilleo's model [10] assuming that all Cu^{2+} ions remain on B-sites, are presented. It can be seen that there is a large deviation between the calculated Curie temperatures and those obtained experimentally, indicating that not all the Cu^{2+} ions go to B-sites but that they are distributed over A- and B-sites. The Curie temperatures of quenched samples are considerably lower than those of slow-cooled ones and also show a decrease with increasing Zn content in $Cu_xZn_{1-x}Fe_2O_4$ quenched and slow-cooled samples.

$CuFe_2O_4$ shows a tetragonal structure at lower temperatures and a cubic one at higher temperatures. $CuFe_2O_4$ is reported to exhibit a cubic structure when quenched from temperatures above 760° C [11], but our studies confirm that this transition temperature lies above 800° C and below 900° C. This is also corroborated by our studies on switching in which samples of $CuFe_2O_4$ quenched from temperatures above 900° C showed memory while the samples of $CuFe_2O_4$ quenched from temperatures of 800, 700 and 600° C showed memory only after switching, the first switching

TABLE II Lattice parameter variation with composition and quenching temperature

Nature of sample	Composition				
	$Cu_{0.8}Zn_{0.2}Fe_2O_4$	$Cu_{0.6}Zn_{0.4}Fe_2O_4$	$Cu_{0.4}Zn_{0.6}Fe_2O_4$	$Cu_{0.2}Zn_{0.8}Fe_2O_4$	$ZnFe_2O_4$
Quenched from 800° C	8.367 Å	8.387 Å	8.412 Å	8.420 Å	8.439 Å
Quenched from 700° C	8.373 Å	8.392 Å	8.414 Å	8.419 Å	8.436 Å
Quenched from 600° C	8.380 Å	8.397 Å	8.413 Å	8.423 Å	8.437 Å
Slow cooled from 950° C	8.385 Å	8.398 Å	8.414 Å	8.427 Å	8.438 Å

TABLE III Curie temperatures and cation distribution for slow-cooled and quenched $Cu_xZn_{1-x}Fe_2O_4$ samples

Samples	History of samples	Currie temperatures from Gilleo model	Curie temperatures from experiment	Cation distribution from experimental values of Curie temperatures
$CuFe_2O_4$	Slow-cooled	455° C	430° C	$(Cu^{2+}_{0.15}Fe^{3+}_{0.85})^A(Cu^{2+}_{0.85}Fe^{3+}_{1.15})^BO_4$
	Quenched from 800° C	–	360° C	$(Cu^{2+}_{0.25}Fe^{3+}_{0.75})(Cu^{2+}_{0.75}Fe^{3+}_{1.25})^BO_4$
$Cu_{0.8}Zn_{0.2}Fe_2O_4$	Slow-cooled	419° C	350° C	$(Cu^{2+}_{0.15}Zn^{2+}_{0.20}Fe^{3+}_{0.65})^A(Cu^{2+}_{0.65}Fe^{3+}_{1.35})^BO_4$
	Quenched from 800° C	–	260° C	$(Cu^{2+}_{0.28}Zn^{2+}_{0.2}Fe^{3+}_{0.52})^A(Cu^{2+}_{0.52}Fe^{3+}_{1.48})^BO_4$
$Cu_{0.6}Zn_{0.4}Fe_2O_4$	Slow-cooled	325° C	270° C	$(Cu^{2+}_{0.06}Zn^{2+}_{0.40}Fe^{3+}_{0.54})^A(Cu^{2+}_{0.54}Fe^{3+}_{1.46})^BO_4$
	Quenched from 800° C	–	150° C	$(Cu^{2+}_{0.20}Zn^{2+}_{0.40}Fe^{3+}_{0.40})^A(Cu^{2+}_{0.4}Fe^{3+}_{1.6})^BO_4$
$Cu_{0.4}Zn_{0.6}Fe_2O_4$	Slow-cooled	162° C	100° C	$(Cu^{2+}_{0.06}Zn^{2+}_{0.60}Fe^{3+}_{0.34})^A(Cu^{2+}_{0.34}Fe^{3+}_{1.66})^BO_4$
	Quenched from 800° C	–	80° C	$(Cu^{2+}_{0.05}Zn^{2+}_{0.6}Fe^{3+}_{0.35})^A(Cu^{2+}_{0.35}Fe^{3+}_{1.65})^BO_4$
$Cu_{0.2}Zn_{0.8}Fe_2O_4$	Slow-cooled	–55° C	–	–

voltage being a function of the quenching temperature [12].

The tetragonal distortion in $CuFe_2O_4$ occurs as a result of a heavy concentration of distorting Cu^{2+} cations at the octahedral sites (B-sites), as evidenced in Table III. The concentrations of Cu^{2+} ions at B-sites is affected by temperature; becoming less and less for higher and higher temperatures. When the samples are quenched from elavated temperatures the cation distribution is frozen-in. When more than 25% of the Cu^{2+} ions migrate to A-sites, the tetragonal structure becomes cubic. Hence c/a values show temperature dependence.

Samples of $Cu_xZn_{1-x}Fe_2O_4$ ($x \neq 1$), slow-cooled and quenched, exhibit a cubic structure. The cation distribution given in Table III shows that in all these samples the concentration of Cu^{2+} ions at B-sites is less than 75%. Hence, these samples do not exhibit tetragonal distortion of the lattice and show a cubic structure.

The linear increase in a with the addition of Zn^{2+} in $Cu_xZn_{1-x}Fe_2O_4$ can be attributed to the atomic volume differences wherein the atomic sizes do not appear to show any relaxation.

In $Cu_{0.8}Zn_{0.2}Fe_2O_4$ samples more Cu^{2+} ions are transferred to A-sites on addition of Zn and on quenching the sample from 800° C compared with the transfer of Cu^{2+} ions in the slow-cooled and quenched $Cu_{0.6}Zn_{0.4}Fe_2O_4$ samples. Hence, on quenching $Cu_{0.8}Zn_{0.2}Fe_2O_4$ samples, the lattice parameter shows a larger change than the $Cu_{0.6}Zn_{0.4}Fe_2O_4$ sample. As there is no significant transfer of Cu^{2+} ions to B-sites on quenching the remaining samples, the lattice parameter also does not show a detectable change.

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Comments upon a statistical model of strength

Recently, a general expression for the failure probability of a brittle material, based upon the presumed knowledge of the flaw-size distribution in the material, was formulated by Jayatilaka and Trustrum [1]. The resulting strength distribution was compared to the standard one given by Weibull [2]. Subsequently, Rickerby [3] extended this analysis to the case where a bimodal flaw distribution is existant in the material. He obtained the first correction to the Weibull distribution in the low strength regime.

In this note, several comments are made with regard to the applicability of these results in the low and high strength regimes.

Jayatilaka and Trustrum [1] obtained the following expression for the cumulative failure probability, P_f, for a system containing N cracks:

$$P_f = 1 - [1 - F(\sigma)]^N, \tag{1a}$$

where

$$F(\sigma) = \int_0^x du \left(1 - \frac{u}{x}\right) \frac{u^{n-2} e^{-u}}{(n-2)!} \tag{1b}$$

and

$$x \equiv \sigma^2 \frac{\pi c}{K_{IC}^2}. \tag{1c}$$

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