

SYNTHESIS AND NEEL TEMPERATURE DETERMINATION OF FERRITES FROM THE CuO–ZnO–Fe₂O₃ SYSTEM

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Abstract

Conditions were established and individual and mixed ferrites with the general formula Cu_xZn_{1-x}Fe₂O₄ ($x = 0; 0.1; 0.2; 0.3; 0.4; 0.5; 0.6; 0.7; 0.8; 1.0$) were synthesized from the CuO–ZnO–Fe₂O₃ system. X-ray phase analysis, Mössbauer spectroscopy and microscopic examinations revealed that the obtained ferrites are monophase samples.

A magnetic device was attached to the Q-Derivatograph (MOM, Hungary) and successfully used for sample investigation in a magnetic field, and in particular for Curie (Neel) temperature determination. The ferrite composition and the thermal treatment conditions were shown to correlate with the Neel temperature of the synthesized ferrites.

Keywords: CuO–ZnO–Fe₂O₃ system, ferrites, Neel temperature

Introduction

The mixed ferrites of zinc with manganese, magnesium, lithium, nickel, etc. have found wide-ranging application in modern radiotechnical, automation, computer and video techniques [1–3]. Less attention has been paid to the mixed copper–zinc ferrites [4–7]. Their study is of importance, however, for the preparation of new magnetic materials and for elucidation of the kinetics and mechanism of their formation in the processing of natural complex copper–zinc raw materials [8, 9].

The copper ferrite CuFe₂O₄ has unique properties as compared to the other ferrites [10, 11]. Its stable low-temperature phase is an inverse spinel. The Cu²⁺ occupies mainly octahedral B sites, while the Fe³⁺ populates B sites and tetrahedral A sites in approximately equal amounts.

The cation distribution of CuFe₂O₄ over non-equivalent sites is variable and strongly dependent on temperature [11]. A Jahn-Teller type distortion of the sites has been observed, due to the presence of Cu²⁺. This leads to more distinct non-equivalent sites than in other spinels.

The zinc ferrite ZnFe_2O_4 , in contrast with CuFe_2O_4 , is a normal spinel [7] and the Zn^{2+} occupies mainly tetrahedral A sites. Moreover, at room temperature (T_R), ZnFe_2O_4 is in a paramagnetic state, whereas CuFe_2O_4 is in a ferrimagnetic state [11]. The mixed ferrites of the $\text{CuO-ZnO-Fe}_2\text{O}_3$ system are to be expected to possess many important properties not found in most of the binary oxides.

The instruments for thermal analysis allow different measurements simultaneously [12–15]. Some of them can be used for Curie (Neel) temperature determination [14, 15].

In this connection, the aim of the present work was to synthesize individual and mixed ferrites of copper and zinc, to investigate the thermal magnetic transition and to determine the Neel temperatures of the ferrites obtained.

Experimental

On the basis of the conditions established earlier [16], copper–zinc ferrites of the type $\text{Cu}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.1; 0.2; 0.3; 0.4; 0.5; 0.6; 0.7; 0.8; 1.0$) were synthesized by using a ceramic technology. They were produced at 1000°C for 300 min, and quenched in water. They are stable compounds which do not change or dissociate when heated to 1200°C . No changes were observed in their TG and DTG curves.

X-ray phase analysis was performed with a TUR-M62 apparatus, using CoK_α radiation and an iron target. Mössbauer spectra were recorded with a standard Mössbauer spectrometer working at the constant acceleration of the ^{57}Co source in a Pd matrix.

To determine the Neel temperatures of the copper and zinc ferrites, a device was constructed for attachment to the Q-Derivatograph (MOM, Hungary), applied for differential thermal and thermogravimetric analysis. In addition to the conventional measurements of temperature, enthalpy, sample mass change and mass rate change, this device allows Curie (Neel) temperature determination on the basis of the magnetic interaction between the sample and the magnetic field induced by the device.

Results and discussion

The X-ray phase analyses and microscopic observations showed that monophasic samples were obtained. The ferrite cubic crystal lattice parameter decreased linearly from 0.8444 nm for ZnFe_2O_4 to 0.8386 nm for CuFe_2O_4 .

The Mössbauer spectra of the ferrites $\text{Cu}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ obtained at T_R displayed a smooth change in type, from two sextets at $x=1$ to a doublet at $x=0$ (Fig. 1). Zinc substitution into CuFe_2O_4 led to the occurrence of a paramagnetic

component, which predominated at $x < 0.4$. The $P(H)$ distribution changed its mean width with increase of x .

At T_R , a substructure was observed in the $P(H)$ distribution; this can be explained by the model of superparamagnetic behavior. The change in $P(H)$ distribution is probably connected with the mean radius (r) of correlation of the hyperfine magnetic interactions.

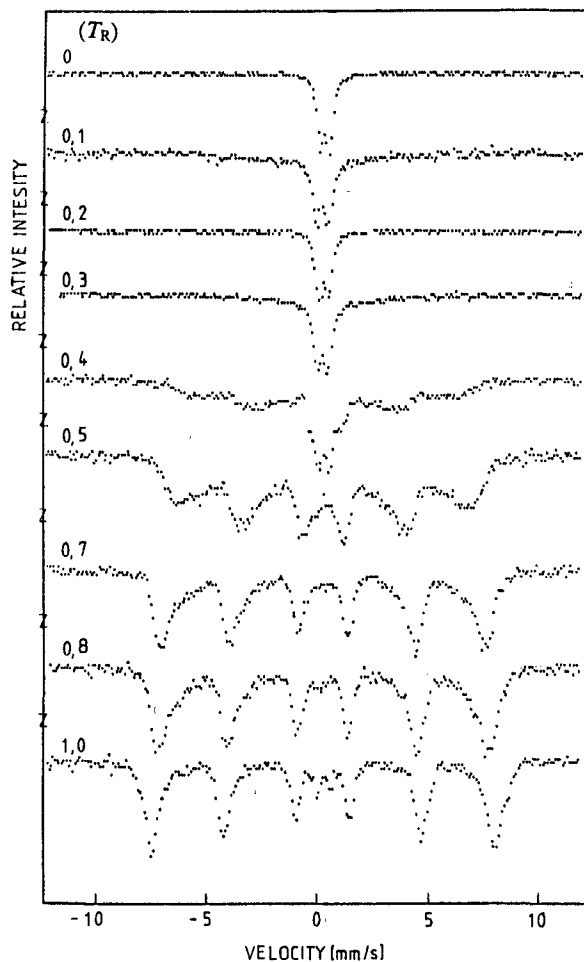


Fig. 1 Mössbauer spectra of ferrites $\text{Cu}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ at room temperature (T_R) and different values of x

As a result of the magnetic interaction between the sample and the magnetic field induced by the device (Fig. 2), an imaginary 'increase' in the magnetic material mass was observed at T_R [17]. With the increase of temperature and the

transition from a ferromagnetic (ferrimagnetic) to a paramagnetic state, the sample 'lost' mass, this loss being terminated at the end of the transition [13–15]. Through use of an internal quartz tube of different length, it is possible to alter the distance between the magnet and the sample, which affects the attractive force.

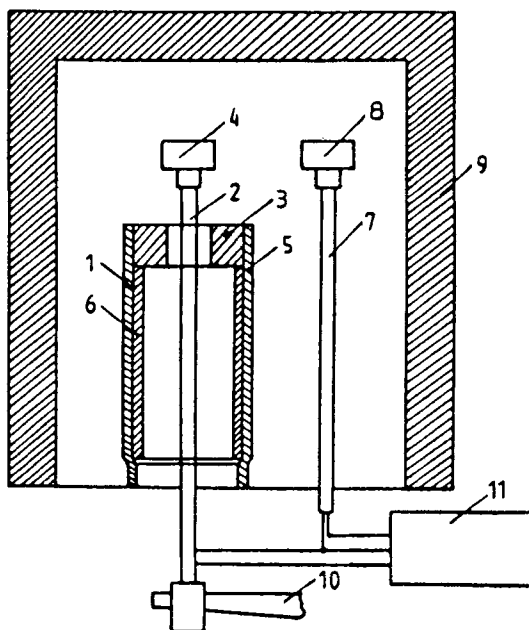


Fig. 2 Illustration of the magnetic device: 1 magnetic keeper; 2, 7 thermocouples; 3 constant magnet; 4, 8 platinum crucibles; 5, 6 external and internal quartz tubes; 9 electric furnace; 10 balance; 11 recorder

The magnetic phase transitions and the corresponding temperatures were determined from the mass curves as functions of temperature. The DTA and DTG curves determine the enthalpy change, and the rate of mass change or the transition rate. The thermobalance was calibrated with reference materials [13–15, 18, 19].

The thermogravimagnetic (TGM) and differential thermogravimagnetic (DTGM) curves of CuFe_2O_4 are shown in Figs 3 and 4. It is seen that with the increase of temperature all the samples 'decreased' in mass. The apparatus sensitivity was high when the constructed device was used. This is evident from the sample mass 'decrease', which exceeds the real mass (20 mg) several times.

When quenched from 1000°C , the CuFe_2O_4 obtained has a cubic crystalline structure [10, 11]. In contrast with other investigated ferrites, two transitions to a paramagnetic state are observed here, having maximum rates at 445 and 475°C , as estimated by DTGM_1 . The transition rate is significantly higher at

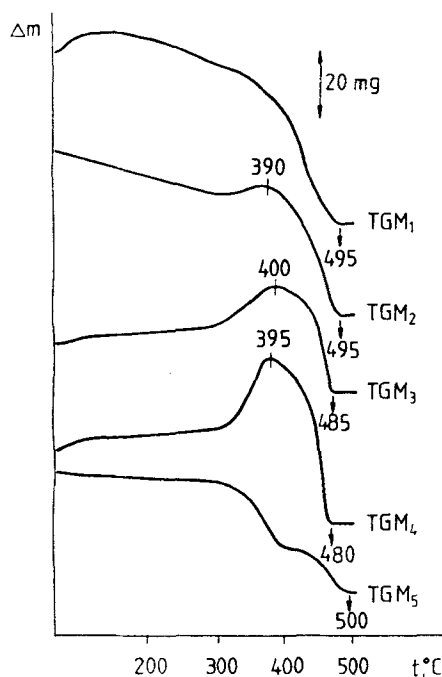


Fig. 3 Thermogravimagnetic curves (TGM) of CuFe_2O_4 : 1 quenched from 1000°C ; 2, 3, 4, 5 slow cooling from 500, 800, 1000 and 1200°C , respectively

445°C . The TGM_1 curve alone is hardly conclusive as to the two-step character of the investigated copper ferrite transition to a paramagnetic state. This conclusion was possible when DTGM curves too were obtained.

The additional investigations showed that only cubic CuFe_2O_4 has a two-step character of transition from a ferrimagnetic to a paramagnetic state. A clearly expressed transition at 500°C was observed when a tetragonal CuFe_2O_4 was studied under the same conditions [17].

A probable explanation for the two transitions of cubic CuFe_2O_4 to the paramagnetic state is to be found in its nonstable, temperature-dependent crystal lattice [10, 11]. If the low-temperature transition at 445°C ($\text{DTGM}_{1,2}$) is due to cubic CuFe_2O_4 , the transition at higher temperature (475 – 485°C) is probably related to the tetragonal phase obtained. The transition from a paramagnetic to a ferrimagnetic state when all CuFe_2O_4 samples are cooled always occurs in only one step, at 500°C , and confirms this suggestion.

The two-step character of the transition is not so clearly expressed when cubic CuFe_2O_4 samples are heated for a second time. In thermal treatment intended to obtain one-phase tetragonal copper ferrite, the investigated samples exhibit only one transition to a paramagnetic state.

When the magnetic device attached to the DTA and TGA apparatus was used, the experimental data increased significantly, as confirmed for samples of CuFe_2O_4 , heated to 500°C (Figs 3 and 4, curves with index 2), 800°C (3), 1000°C (4) and 1200°C (5), and then slowly cooled to T_R .

At the first three temperatures, some 'increase' in sample mass is observed, which is highest for the sample heated to 1000°C (ca 24 mg). The maximum in this 'increase' is at ca 400°C . The TGM curves show that the slowly cooled samples undergo internal structural changes, which increase the force of interaction between the sample and the magnetic field, leading to an apparent mass increase.

On heating to 1200°C and subsequent cooling, no process of mass 'increase' is observed. This indicates that at this temperature a stable magnetic structure is formed which is little influenced by the change of temperature.

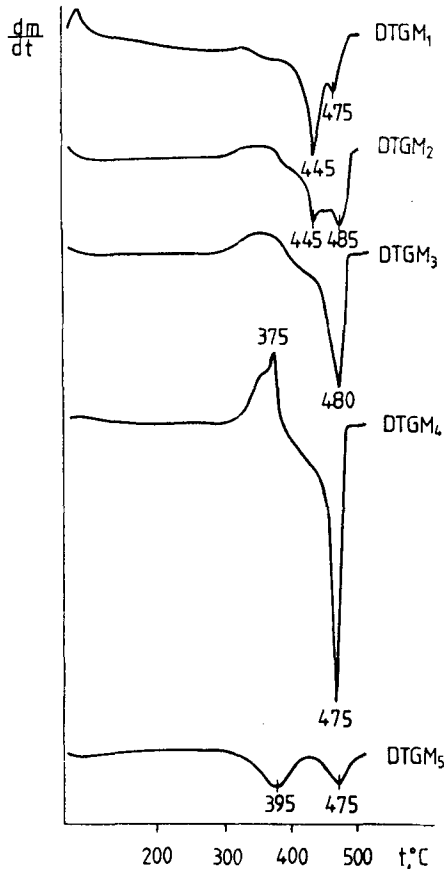


Fig. 4 Differential thermogravimagnetic curves (DTGM) of CuFe_2O_4 : 1 quenched from 1000°C ; 2, 3, 4, 5 slow cooling from 500 , 800 , 1000 and 1200°C , respectively

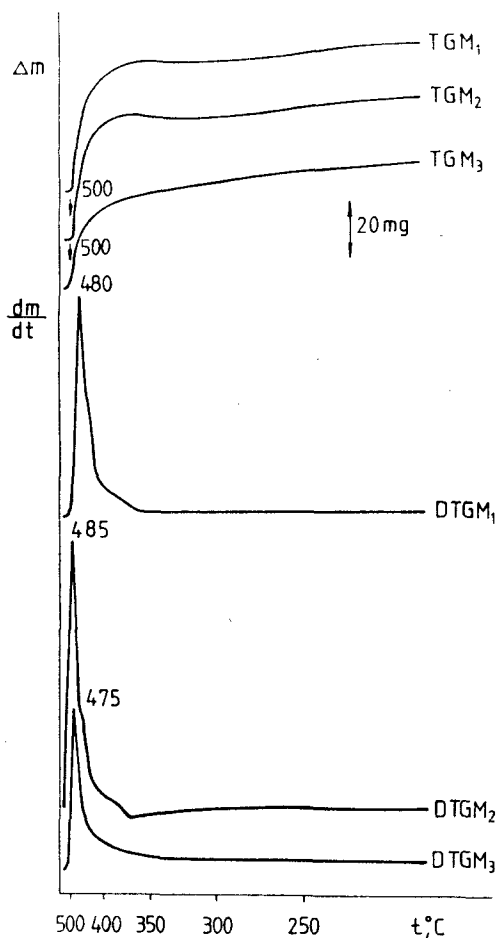


Fig. 5 TGM and DTGM curves of CuFe_2O_4 , recorded on cooling samples 1, 2 and 5 from Figs 3 and 4

Increase of the sample heating temperature leads to changes in the DTGM curves, too (Fig. 4). For the initial sample and that heated to 500°C , two clearly expressed minima were established in the DTGM₁ and DTGM₂ curves, whereas the following two curves displayed an intense minimum at $475\text{--}480^\circ\text{C}$ and a maximum proportional to the rate of sample 'increase' at $350\text{--}375^\circ\text{C}$.

The sample heated to 1200°C again yielded two minima in the DTGM₅ curve, corresponding to two different rates (probably differing in character) of the transition to a paramagnetic state.

In the TGM and DTGM curves recorded on cooling from 500°C to T_R , irrespective of the preliminary thermal treatment, all the samples exhibited a smooth mass 'increase' and only one sharp maximum in the DTGM curves

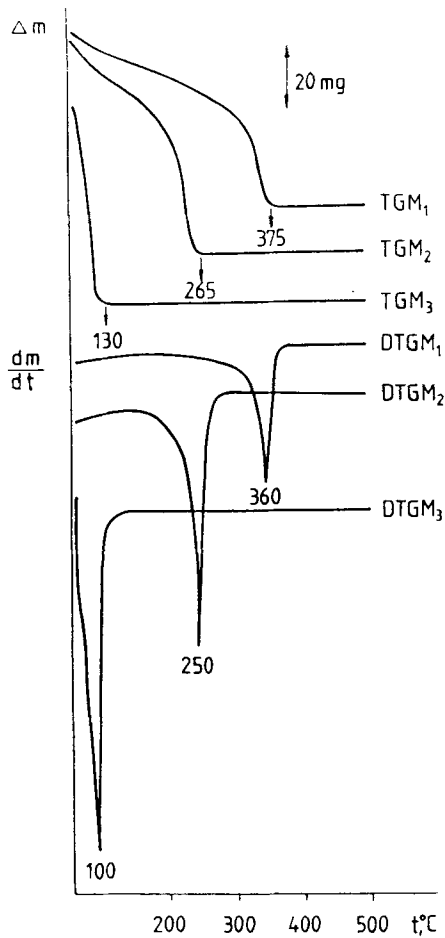


Fig. 6 TGM and DTGM curves of mixed ferrites $\text{Cu}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$: 1- $x=0.8$; 2- $x=0.6$; 3- $x=0.4$

(Fig. 5). This confirms the conclusion that at T_R the magnetic structure of CuFe_2O_4 is rather different from that occurring when samples are heated or cooled. Inasmuch as the ferrites are utilized in mechanisms operating at room temperature, it is clear that use of the magnetic device results in more complete and significantly more comprehensive data.

Figure 6 depicts TGM and DTGM curves of samples of mixed ferrites $\text{Cu}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ ($x=0.4$; 0.6 ; 0.8). A decrease in Neel temperature is observed with increase of zinc content. The values obtained differ both from those given in the literature [4-6] and from those estimated by the model of Gileo [20].

It is interesting that the DTGM curves contain only one minimum, which is very well expressed. The mass of the mixed ferrite samples (10 mg) is half that of CuFe_2O_4 (20 mg), all other experimental conditions being the same. Comparison of the TGM curves in Figs 3 and 6 reveals that zinc substitution in copper ferrite improves the magnetic properties. At $x < 0.3$ and T_R , the ferrites are in a paramagnetic state, as confirmed by the Mössbauer spectra.

Conclusions

1. A magnetic device was attached to the Q-Derivatograph (MOM, Hungary) and successfully used for sample investigation in a magnetic field, and in particular for Curie (Neel) temperature determination.

2. The conditions of thermal treatment of copper ferrite, CuFe_2O_4 , affect its magnetic structure significantly. This is related to different rates of transition from a ferrimagnetic to a paramagnetic state, to different Neel temperatures, to changes in the magnetic properties on heating. The observed Neel temperatures lie in the range 480–500°C.

3. The mixed copper-zinc ferrites $\text{Cu}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ with $x > 0.4$ exhibit a clearly expressed transition from a ferrimagnetic to a paramagnetic state, the rate of this transition being increased and the magnetic properties improved when the zinc content is elevated.

References

- 1 Yu. D. Tretyakov, *Izv. Akad. Nauk SSSR, Neorg. Materialy*, 21 (1985) 693.
- 2 M. J. Ruthner, *Ferrites, Proceedings of the 3rd International Conference of Ferrites, Center for Academic Publication, Japan 1981*, p. 64.
- 3 M. P. Bogdanovich, *Fizika Tverdogo Tela*, 33 (1991) 3476.
- 4 S. R. Sawant and R. N. Patil, *J. Mater. Sci.*, 16 (1981) 3496.
- 5 R. G. Kulkarni and V. U. Patil, *J. Mater. Sci.*, 17 (1982) 843.
- 6 S. R. Sawant and R. N. Patil, *Ind. J. Pure and Applied Phys.*, 20, 5 (1982) 353.
- 7 A. A. E. Bellini, A. M. Abdel-Badei and El-H. M. Dietallah, *Thermochim. Acta*, 165 (1990) 147.
- 8 B. Boyanov, R. Dimitrov and N. Dobrev, *Tsvetnye Metally*, 5 (1986) 34.
- 9 R. Dimitrov, B. Boyanov and S. Nikolov, *Thermochim. Acta* 34 (1979) 149.
- 10 B. J. Evans and S. S. Hafner, *J. Phys. Chem. Sol.*, 29 (1968) 1573.
- 11 B. J. Evans, S. S. Hafner and G. M. Kalvius, *Phys. Letters*, 23 (1966) 24.
- 12 J. Paulik, F. Paulik and M. Arnold, *J. Thermal Anal.*, 32 (1987) 31.
- 13 P. K. Gallagher and E. M. Gyorgy, *Thermochim. Acta*, 109 (1986) 103.
- 14 P. K. Gallagher, E. Coleman, S. Jin and R. C. Sherwood, *Thermochim. Acta*, 37 (1980) 291.
- 15 P. Myslinski, W. Precht and J. Staskiewicz, *J. Thermal Anal.* 35 (1989) 193.
- 16 B. Boyanov, *J. Plovdiv Univ. (Bulg.)* 24 (1986) 306.
- 17 B. Boyanov, *Zavodskaya Lab.*, 3 (1990) 43.
- 18 A. Langier-Kuzniarowa, *J. Thermal Anal.*, 29 (1984) 913.
- 19 S. D. Norem, N. J. O'Neil and A. P. Gray, *Thermochim. Acta*, 1 (1970) 29.
- 20 M. A. Gileo, *J. Phys. Chem. Sol.*, 13 (1960) 33.

Zusammenfassung — Die Bedingungen im System $\text{CuO-ZnO-Fe}_2\text{O}_3$ wurden ermittelt und Einzel- als auch Mischferrite der allgemeinen Formel $\text{Cu}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ (mit $x = 0; 0.1; 0.2; 0.3; 0.4; 0.5; 0.6; 0.7; 0.8; 1.0$) hergestellt. Röntgenphasenanalyse, Mössbauerspektroskopie und mikroskopische Untersuchungen ergaben, daß es sich bei den erhaltenen Ferriten um Monophasenproben handelt.

Einem Q-Derivatographen (MOM, Hungary) wurde eine Magneiteinheit angeschlossen und erfolgreich für die Untersuchung der Proben in einem magnetischen Feld, im speziellen für die Bestimmung des Curie-Punktes eingesetzt. Es wurde die Korrelation zwischen den Bedingungen für die thermische Behandlung und dem Curie-Punkt der hergestellten Ferrite gezeigt.