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# SYNTHESIS AND NEEL TEMPERATURE DETERMINATION OF FERRITES FROM THE MO–ZnO–$Fe_2O_3$ SYSTEMS ($M$=Cu, Co AND Ni)

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## Abstract

The Curie (Neel) temperature is successfully determined by means of a simple magnetic device attached to the Q Derivatograph (MOM, Hungary), which is widely used in many laboratories. This possibility is demonstrated by a study of ferrite materials with general formula $M_xZn_{1-x}Fe_2O_4$ ($M$=Cu, Co and Ni; $x$=0.0; 0.2; 0.4; 0.5; 0.6; 0.8; 1.0). X-ray phase analysis, Mössbauer spectroscopy and microscopic examinations revealed that the obtained ferrites are monophase samples.

The mixed ferrites possess more strongly expressed magnetic properties than those of the individual ferrites; the maximum magnetic interaction in these ferrites is observed at different zinc contents.

**Keywords:** cobalt, copper, ferrites, Neel temperature, nickel

## Introduction

The mixed ferrites of zinc with copper, cobalt, nickel, magnesium, manganese, lithium, etc. have found wide-ranging application, e.g. in high-frequency inductors, transformers, memory cores and read/write heads. The techniques of preparation and the type of substitution affect their physical and chemical properties [1–6].

A number of investigators have studied the influence of copper [3, 4, 7], cobalt [8–10] and nickel [11–14] substitution on the properties of zinc ferrite. The effects of zinc substitution on the electrical and physical properties of nickel and cobalt ferrites have been studied by others [15, 16]. However, less attention has been paid to determination of the Neel temperatures of the mixed ferrites, these temperatures being connected with their cation distribution [17].

The present work deals with the thermal magnetic transitions and determination of the Neel temperatures of ferrites obtained by using a DTA and TG apparatus.

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## Experimental

Ferrites of the type $M_xZn_{1-x}Fe_2O_4$ ($M$=Cu, Co and Ni; $x$=0.0; 0.2; 0.4; 0.5; 0.6; 0.8; 1.0) were synthesized by using a standard ceramic technique [18]. The Cu–Zn ferrites were obtained by heating at 1000°C for 300 min, followed by quenching in water. Their properties were described and discussed in detail in [19]. The Co–Zn and Ni–Zn ferrites were synthesized at 1200°C for 300 min, with subsequent slow cooling to room temperature.

X-ray diffraction patterns for all individual and mixed ferrites were obtained by using $CoK_\alpha$ radiation, and the lattice constants were calculated. Mössbauer spectra were recorded with a standard transmission Mössbauer spectrometer working at the constant acceleration of the $^{57}Co$ source in a Pd matrix.

For determination of the Neel temperatures of the ferrites, a device has been constructed for attachment to an apparatus for differential thermal and thermogravimetric analysis, the Q Derivatograph (MOM, Hungary). Two variants of this device were described earlier [19, 20]. In addition to 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.

As a result of this interaction, an imaginary "increase" in magnetic material mass is observed at room temperature. With increase of temperature and the transition from a ferromagnetic (ferrimagnetic) to a paramagnetic state, the sample "loses" mass, this loss being terminated at the end of the transition. The thermobalance was calibrated by using several reference materials [21, 22].

The magnetic phase transitions and the corresponding temperatures are determined from the mass curve as functions of temperature. The DTA and DTG curves reveal the enthalpy change, and the rate of mass change or the transition rate.

## Results and discussion

X-ray phase analysis and microscopic observations, showed that monophase samples were obtained. The ferrite cubic crystal lattice parameter ($a$) uniformly decreased from 0.8444 nm for $ZnFe_2O_4$ to 0.8386 nm for $CuFe_2O_4$, 0.8385 nm for $CoFe_2O_4$ and 0.8332 nm for $NiFe_2O_4$ (Tables 1 and 2). The values obtained are very close to data in the literature [16, 23].

The Mössbauer spectra of the ferrites $M_xZn_{1-x}Fe_2O_4$, obtained at room temperature ($T_R$), indicated a smooth change in local magnetic structure with change of $M^{2+}$ concentration ($x$) (Figs 1 and 2).

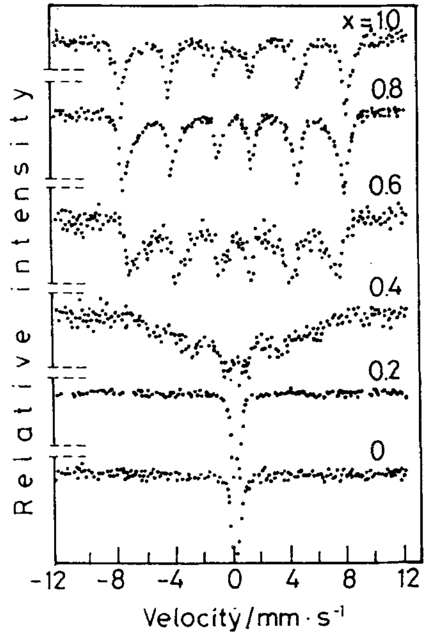

Fig. 1 Mössbauer spectra of ferrites of the type $Co_xZn_{1-x}Fe_2O_4$ at room temperature ($T_R$) and different values of ($x$)

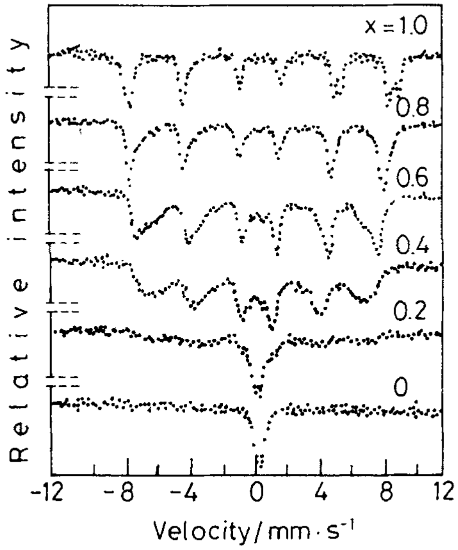

Fig. 2 Mössbauer spectra of ferrites of the type $Ni_xZn_{1-x}Fe_2O_4$ at room temperature ($T_R$) and different values of ($x$)

$Cu^{2+}$, $Co^{2+}$ and $Ni^{2+}$ occupy mainly octahedral (B) sites in the spinel lattice, whereas $Zn^{2+}$ occupies tetrahedral (A) sites. $CuFe_2O_4$, $CoFe_2O_4$ and $NiFe_2O_4$ are inverse spinels, while $ZnFe_2O_4$ is a normal one. In $M_xZn_{1-x}Fe_2O_4$, the ferrimagnetic ordering of the cation spins increases with increase of $x$. The reason is that $M^{2+}$ is magnetic, and thus, as $x$ increases, the strength of the A–B exchange interaction, responsible for the ferrimagnetic ordering, also increases. At $x>0.8$, the magnetic ordering predominates and the spectra obtained are sextets, whereas at $x<0.2$ the ordering vanishes completely and the spectra are doublets.

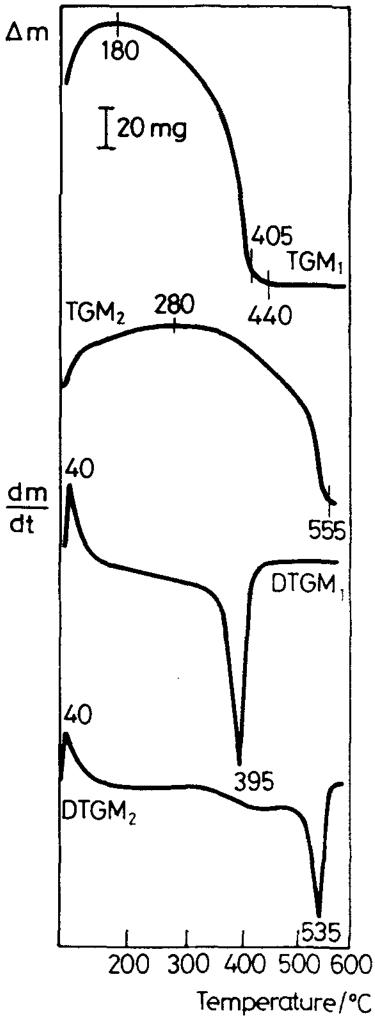

**Fig. 3** Thermogravimagnetic (TGM) and differential thermogravimagnetic (DTGM) curves of $Co_{0.8}Zn_{0.2}Fe_2O_4$ (1) and $CoFe_2O_4$ (2)

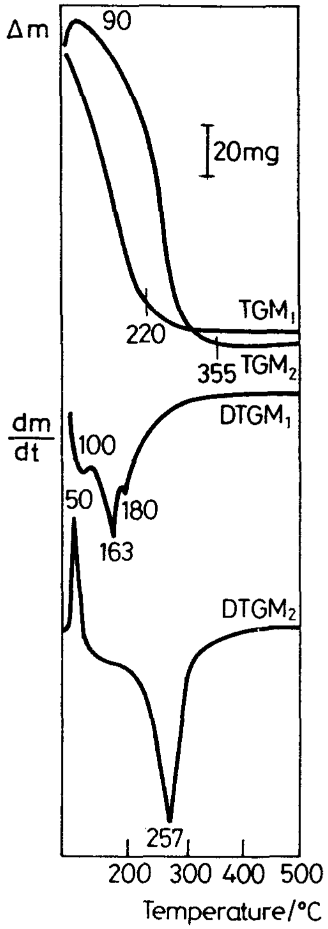

**Fig. 4** Thermogravimagnetic (TGM) and differential thermogravimagnetic (DTGM) curves of $Co_{0.5}Zn_{0.5}Fe_2O_4$ (1) and $Co_{0.6}Zn_{0.4}Fe_2O_4$ (2)

The Mössbauer spectra observed for $M_xZn_{1-x}Fe_2O_4$ are similar to those for the ferrite $Cu_{0.5}Zn_{0.5}Fe_2O_4$, depending on temperature [3]. The variation in P(H) distribution can be explained by the model of superparamagnetic behaviour.

All ferrites obtained in this study are stable compounds, neither changing nor dissociating when heated to 1200°C. The TG and DTG curves of the ferrites revealed no changes. The picture was rather different when the magnetic device was used. The thermogravimagnetic (TGM) and differential thermogravimagnetic (DTGM) curves [19, 25] of $Co_xZn_{1-x}Fe_2O_4$ and $Ni_xZn_{1-x}Fe_2O_4$ are shown in Figs 3–7. All samples are seen to "decrease" in mass as the temperature rises. The apparatus sensitivity is high when the constructed device is used. This is evident from the mass "decrease" of the samples, which exceeds their real mass (20 mg) several times.

The data obtained on $Co_xZn_{1-x}Fe_2O_4$ are listed in Table 1, and those on $Ni_xZn_{1-x}Fe_2O_4$ in Table 2. The results permit the following general conclusions.

Cobalt–zinc ferrites behave differently in a magnetic field, depending on the zinc content. On heat treatment, the first three investigated ferrites (Table 1) "increase" in mass, the maximum moving to lower temperatures, corresponding to decreasing $x$. This is obvious from the TGM and DTGM curves in Figs 3 and 4. The observed process is probably due to additional magnetic ordering of the crystal lattice ions leading to an increase in the induced magnetic field.

Such an "imaginary" ferrite mass increase is not found at $x<0.5$. The ferrites with higher zinc contents have DTGM curves with one clearly expressed minimum corresponding to the highest rate of magnetic transition.

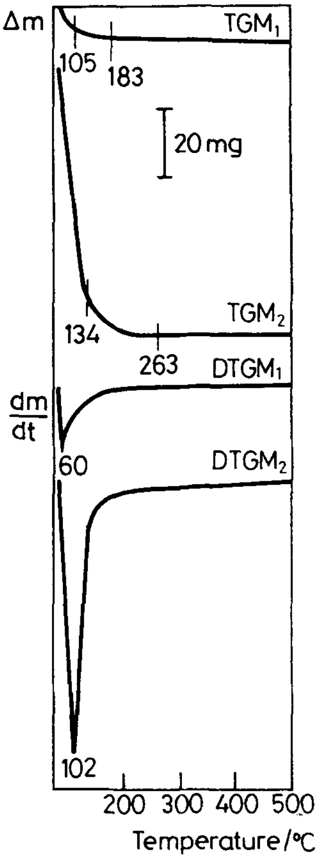

**Fig. 5** Thermogravimagnetic (TGM) and differential thermogravimagnetic (DTGM) curves of $Co_{0.2}Zn_{0.8}Fe_2O_4$ (1) and $Co_{0.4}Zn_{0.6}Fe_2O_4$ (2)

**Table 1** Structural, magnetic and thermogravimagnetic properties of $Co_xZn_{1-x}Fe_2O_4$

| N | Ferrite | *a* / | "+$\Delta m$" at *t* | | | total "$-\Delta m$" at $T_N$ | | $T_N$ / °C | |
|---|---|---|---|---|---|---|---|---|---|
| | | nm | mg | % | °C | mg | % | our data | [24] |
| 1 | $CoFe_2O_4$ | 0.8385 | 22 | 110 | 280 | 60 | 300 | 555 | 500 |
| 2 | $Co_{0.8}Zn_{0.2}Fe_2O_4$ | 0.8390 | 24 | 120 | 180 | 82 | 410 | 440 | 386 |
| 3 | $Co_{0.6}Zn_{0.4}Fe_2O_4$ | 0.8400 | 14 | 70 | 90 | 120 | 600 | 355 | 276 |
| 4 | $Co_{0.5}Zn_{0.5}Fe_2O_4$ | 0.8415 | – | – | – | 116 | 580 | 220 | 150 |
| 5 | $Co_{0.4}Zn_{0.6}Fe_2O_4$ | 0.8422 | – | – | – | 106 | 530 | 134 | 83 |
| 6 | $Co_{0.2}Zn_{0.8}Fe_2O_4$ | 0.8434 | – | – | – | 14 | 70 | 105 | – |
| 7 | $ZnFe_2O_4$ | 0.8440 | – | – | – | – | – | – | – |

**Table 2** Structural, magnetic and thermogravimagnetic properties of $Ni_xZn_{1-x}Fe_2O_4$

| N | Ferrite | *a* / | total "$-\Delta m$" at $T_N$ | | $T_N$ / °C | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | nm | mg | % | our data | A | B | C | D | L |
| 1 | $NiFe_2O_4$ | 0.8332 | 86 | 300 | 595 | 565 | 570 | 570 | 560 | 585 |
| 2 | $Ni_{0.8}Zn_{0.2}Fe_2O_4$ | 0.8350 | 130 | 650 | 512 | 495 | 480 | 466 | 466 | 530 |
| 3 | $Ni_{0.6}Zn_{0.4}Fe_2O_4$ | 0.8381 | 114 | 570 | 495 | 425 | 345 | 350 | 350 | 435 |
| 4 | $Ni_{0.5}Zn_{0.5}Fe_2O_4$ | 0.8393 | 112 | 560 | 375 | 370 | 285 | 280 | 270 | 350 |
| 5 | $Ni_{0.4}Zn_{0.6}Fe_2O_4$ | 0.8409 | 92 | 460 | 344 | 330 | 215 | 180 | 200 | 295 |
| 6 | $Ni_{0.2}Zn_{0.8}Fe_2O_4$ | 0.8420 | 62 | 310 | 332 | 275 | 80 | 100 | 70 | 85 |

A, B, C and D – different methods of ferrite synthesis

L – literature data quoted in [1]

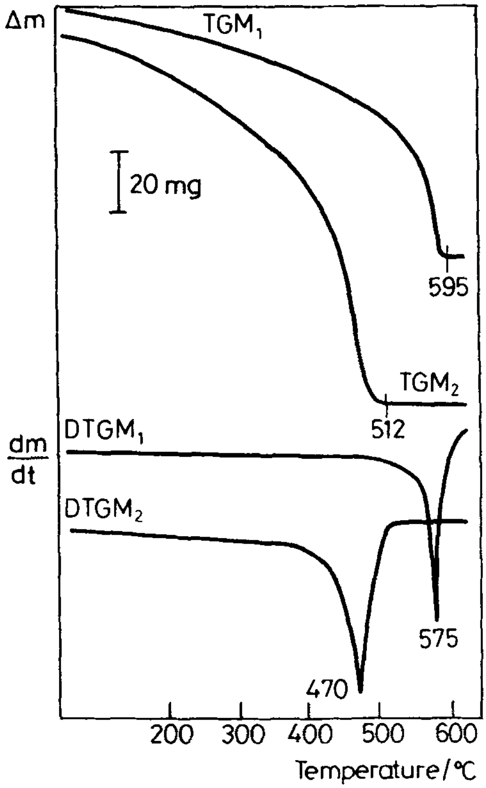

**Fig. 6** Thermogravimagnetic (TGM) and differential thermogravimagnetic (DTGM) curves of $NiFe_2O_4$ (1) and $Ni_{0.8}Zn_{0.2}Fe_2O_4$ (2)

The transition from a ferrimagnetic to a paramagnetic state is smoother with decrease of $x$ as confirmed by the character of the TGM curves (Figs 4 and 5). Investigation of the ferrite materials with the magnetic device reveals the total "decrease" in sample mass at the Neel temperature (Table 1). This can be accepted as a measure of the magnetic interaction between a magnetic material and the magnetic field. The data show that this interaction changes as a function of $x$, passing through a maximum at $x=0.6$. This is further confirmation that the mixed ferrites possess more interesting properties than those of the individual ferrites.

The data in Table 2 indicate that the nickel–zinc ferrites also behave differently in a magnetic field. In this case, the maximum in "$-\Delta m$" is at $x=0.8$, i.e. it moves to ferrites with a higher nickel content.

Comparison of the $T_N$ data with those reported in the literature demonstrates good agreement, but also certain differences. Our results are close to those reported for the ferrites synthesized according to method A and the published $L$

data [1]. The observed difference, depending on the cation distribution, again confirming the importance of the method used for ferrite synthesis. In this respect, new possibilities might be sought by varying the ceramic technology conditions and also by using coprecipitation methods and variation of the subsequent thermal treatment.

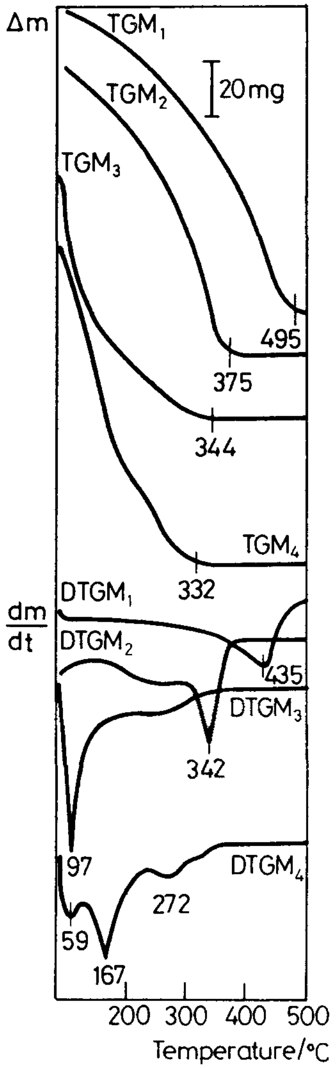

**Fig. 7** Thermogravimagnetic (TGM) and differential thermogravimagnetic (DTGM) curves of $Ni_{0.6}Zn_{0.4}Fe_2O_4$ (1), $Ni_{0.5}Zn_{0.5}Fe_2O_4$ (2), $Ni_{0.4}Zn_{0.6}Fe_2O_4$ (3) and $Ni_{0.2}Zn_{0.8}Fe_2O_4$ (4)

The form of the TGM curves (Figs 6 and 7) indicates that increase of zinc substitution in $NiFe_2O_4$ leads to a smoother transition from a ferrimagnetic to a paramagnetic state. Exact determination of $T_N$ at $x=0.2$ is rather difficult. The DTGM$_4$ curve in Fig. 7 points to three different rates of phase transition, which might be due to different local magnetic structures. This is confirmed by the Mössbauer spectra of $M_xZn_{1-x}Fe_2O_4$. It is evident that, if the nature of the Mössbauer spectrum is between a well-expressed sextet and a doublet, the magnetic phase transition occurs within a temperature range. In this case, the temperature above which the magnetic interaction between the sample and magnetic field is zero can be accepted as $T_N$.

The mixed copper–zinc ferrites exhibit similar behaviour in a magnetic field [19]. $CuFe_2O_4$ may have a cubic or a tetragonal crystal structure, this influencing the TGM and DTGM curves obtained. The cubic form is obtained on quenching from above 1000°C, whereas the tetragonal form is formed on slow cooling of the sample.

A probable explanation for the two transitions of cubic $CuFe_2O_4$ into a paramagnetic state may involve its nonstable, temperature-dependent crystal lattice [4]. While the low-temperature transition at 445°C is due to cubic $CuFe_2O_4$, the transition at higher temperatures (475–485°C) is probably related to the tetragonal phase.

When the magnetic device is used for $T_N$ determination, the results obtained during the cooling of mixed ferrite samples do not differ from those obtained on heating. Under the given experimental conditions, an increase of 5–10 deg is observed in the recorded Neel temperature.

## Conclusions

1. The Curie (Neel) temperature may be successfully determined by means of a simple magnetic device attached to the widely-used Q Derivatograph (MOM; Hungary). This possibility was demonstrated by a study of ferrites with general formula $M_xZn_{1-x}Fe_2O_4$ ($M$=Cu, Co and Ni).
2. The Neel temperatures of the individual ferrites of Cu, Co and Ni and their mixed ferrites with Zn were determined. The synthesis conditions were found to exert a significant effect on $T_N$.
3. The mixed ferrites possess more strongly expressed magnetic properties than those of the individual ferrites; the maximum magnetic interaction was observed at different zinc contents.

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**Zusammenfassung** — Durch Ergänzung des von der ungarischen Firma "MOM" produzierten Gerätes vom Typ "Q-Derivatograph" mittels einer einfachen Magneteinheit konnte die Curie-Temperatur erfolgreich bestimmt werden. Diese Möglichkeit wird anhand der Untersuchung von Ferritsubstanzen der allgemeinen Formel $Me_xZn_{1-x}Fe_2O_4$ ($Me$ = Cu, Co, Ni) mit $x$ = 0.0, 0.2, 0.4, 0.5, 0.6, 0.8 und 1.0 gezeigt. Mittels Röntgen-Phasenanalyse, Mössbauer-Spektroskopie und mikroskopischer Untersuchung wurde gezeigt, daß es sich bei den untersuchten Ferriten um Monophasen-Substanzen handelt.