

## Note

### ON THE THERMAL STABILITY OF $\text{Fe}_2\text{Mn}_{0.5}\text{Zn}_{0.5}(\text{C}_2\text{O}_4)_4$

T. COSEAC<sup>1</sup>, SILVIA BOCAI<sup>2</sup>, MARIA BREZEANU<sup>2</sup> and E. SEGAL<sup>1</sup>

<sup>1</sup>Chair of Physical Chemistry and Electrochemical Technology, Faculty of Chemical Engineering, Polytechnical Institute of Bucharest, Bulevardul Republicii 13, and <sup>2</sup>Chair of Inorganic Chemistry and Technology, Faculty of Chemical Technology, Polytechnical Institute of Bucharest, str. Dumbrava Roşie 23, Bucharest (Romania)

(Received 7 May 1985)

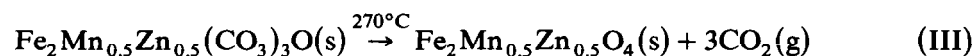
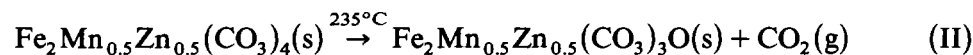
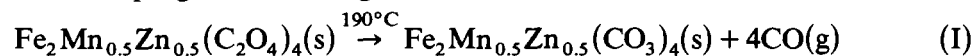
Following our research [1] concerning the thermal stability of polynuclear coordination compounds (PCC) this paper deals with the thermal decomposition of  $\text{Fe}_2\text{Mn}_{0.5}\text{Zn}_{0.5}(\text{C}_2\text{O}_4)_4$  as well as with the crystallization of the cubic ferrite from the mixture of oxides generated through thermolysis of the parent PCC. The kinetic parameters of these processes have been obtained using non-isothermal techniques and the resulting solid phases have been characterised by X-ray diffractometry. The results of an attempt to limit the thermal stability temperature field of the cubic ferrite are equally discussed.

#### EXPERIMENTAL

Powders of  $\text{Fe}_2\text{Mn}_{0.5}\text{Zn}_{0.5}(\text{C}_2\text{O}_4)_4$ , synthesized according to a method described elsewhere [2], were used. The heating curves of powdered samples of Fe–Mn–Zn oxalate have been recorded between 20 and 1000°C in a Paulik–Paulik–Erdey type MOM derivatograph (Budapest) at various heating rates (2.5, 5, 10 K min<sup>-1</sup>). X-ray diffractograms of various samples have been obtained with a Phillips PW 1140/10 diffractometer. In order to obtain the mean crystallite sizes of the parent PCC, Scherrer's formula [3] was applied. The value thus determined is 155Å.

#### RESULTS AND DISCUSSION

According to the TG curves, the following decomposition steps which occur on progressive heating of Fe–Mn–Zn oxalate are indicated



The temperatures written above the arrows correspond to the maximum decomposition rates as shown by the TG and DTG curves. The X-ray diffractograms show that the amorphous state of the powder resulted after the last decomposition step. This amorphous character is exhibited by samples heated at temperatures just below 400°C, while for samples heated between 420 and 560°C the X-ray diffractograms gave lines of the cubic ferrite. The width of these lines decreases on increasing temperature showing an increase of the crystallinity and, thus, of the perfection of the crystalline lattice. An exothermic peak on the DTA curve, at 470°C, equally indicates the crystallization of the cubic ferrite in this temperature range. The X-ray diffractograms of the samples heated at temperatures above 580°C exhibit the cubic ferrite lines as well as the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> lines. The increase in width of the lines suggests the build-up of a new ferritic lattice. At 580°C the transformation of the normal spinel ferritic lattice into the inverse spinel ferritic lattice occurs, its small thermal effect not being recorded on the DTA curve.  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> is probably an intermediate in this phase transition, although iron in excess of the stoichiometric composition of the parent PCC represents an alternative explanation. The absence of the lines of the divalent metal oxides in the X-ray diffractograms supports the last assumption, but the increased dispersion of the powder as well as the reduced concentration of Me<sup>II</sup>O type oxides may equally account for it. In this temperature range the TG curves do not show any weight changes.

The isothermal treatment of the parent PCC followed by X-ray analysis of the resulting solid phase shows that in the range 420–560°C the normal spinel ferritic lattice is stable.

The non-isothermal kinetic parameters (activation energy,  $E$ , pre-exponential factor,  $A$ , and reaction order,  $n$ ) for reactions I, II and III, obtained with the Coats–Redfern method [4] are given in Table 1. The quite satisfactory agreement between the values of the kinetic parameters for the three different heating rates shows no heat transfer limitations.

The value  $n = 1$  actually corresponds to instantaneous nucleation followed by one-dimensional growth of the nuclei.

TABLE 1  
Values of non-isothermal kinetic parameters of the reactions I, II and III

Heating rate (K min <sup>-1</sup> )	Reaction I			Reaction II			Reaction III		
	$E$ (kcal mol <sup>-1</sup> )	$A$ (s <sup>-1</sup> )	$n$	$E$ (kcal mol <sup>-1</sup> )	$A$ (s <sup>-1</sup> )	$n$	$E$ (kcal mol <sup>-1</sup> )	$A$ (s <sup>-1</sup> )	$n$
2.5	36.0	$4.8 \times 10^{14}$	1	52.0	$4.2 \times 10^{19}$	1	53.0	$1.0 \times 10^{19}$	1
2.5	36.5	$3.8 \times 10^{14}$	1	57.4	$5.9 \times 10^{21}$	1	53.0	$3.7 \times 10^{18}$	1
2.5	34.0	$4.8 \times 10^{13}$	1	52.0	$3.6 \times 10^{19}$	1	49.0	$1.2 \times 10^{17}$	1

In DTA, the exothermic peak at 470°C, assigned to the crystallization of the normal spinel ferritic lattice, was used to determine the activation energy,  $E$ , as well as the exponent  $m$ , assuming that the kinetics of the process are described by the following form of the JMAYK equation [5]

$$\frac{d\alpha}{dt} = km(1 - \alpha)t^{m-1} \quad (1)$$

where  $k$  is the kinetic constant and  $m$  a constant which depends on the reaction mechanism and the form of the nuclei. Using Šesták's approximation [6], the following results have been obtained:  $E = 68 \text{ kcal mol}^{-1}$  and  $m = 1.13$ . The value of  $m$  suggests an instantaneous nucleation followed by a diffusion-controlled growth of the nuclei.

## CONCLUSIONS

(1) The normal spinel ferritic lattice is stable in the temperature interval 420–560°C.

(2) The non-isothermal kinetic analysis of the decomposition of Fe–Mn–Zn oxalate as well as of the normal spinel ferritic lattice crystallization shows the validity of the JMAYK equation.

## REFERENCES

- 1 M. Brezeanu, E. Tatu, S. Bocai, O. Brezeanu, E. Segal and L. Patron, *Thermochim. Acta*, 78 (1984) 445.
- 2 M. Brezeanu and S. Bocai, unpublished work.
- 3 A. Guinier, *Théorie et Technique de la Radiocristallographie*, Dunod, Paris, 1964, p. 462.
- 4 A.W. Coats and J.P. Redfern, *Nature (London)*, 201 (1964) 68.
- 5 J. Šesták, *Thermophysical Properties of Solids*, Academia, Prague, 1984, p. 191.
- 6 J. Šesták, *Phys. Chem. Glasses*, 15 (1976) 137.