SOLID STATE REACTIVITY AND MECHANISMS IN OXIDE SYSTEMS
IX. Formation and decomposition of $NiMn_2O_4$, $Ni_{1.5}Mn_{1.5}O_4$ and Mg_2TiO_4 in the metastable state

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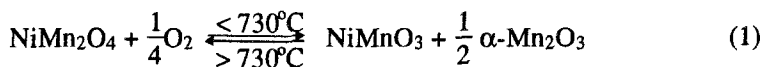
Starting from oxalate mixed crystals $Ni_xMn_{3-x}(C_2O_4)_3 \cdot 6H_2O$ thermal decomposition at reduced oxygen partial pressure ($p_{O_2} = 2\%$) leads to the formation of $NiMn_2O_4$ ($x = 1$) at metastable conditions. $Ni_{1.5}Mn_{1.5}O_4$ ($x = 1.5$) existing in the metastable state only has been also prepared. The spinel compounds both are of the highly inversed type. Following a sol-gel preparation route Mg_2TiO_4 has been also found to be formed in the metastable state. Annealing results in decomposition of the compounds providing $NiMnO_3$ and $1/2\alpha\text{-}Mn_2O_3$ or $NiMnO_3$ only or $MgTiO_3$ and MgO, respectively. The reaction rates observed are lower for $NiMn_2O_4$ and $Ni_{1.5}Mn_{1.5}O_4$ than for Mg_2TiO_4 decomposition. The reverse reaction of $NiMn_2O_4$ formation above 730°C shows an endothermic enthalpy of $+61$ kJ·mol^{-1}. For Mg_2TiO_4 formation above 1050°C an endothermic enthalpy of $+19.3$ kJ·mol^{-1} is found. The results are discussed in terms of structural features of the oxides.

Keywords: Mg_2TiO_4, $NiMn_2O_4$, $Ni_{1.5}Mn_{1.5}O_4$, semiconductor ceramics, solid state reactivity

Introduction

In a previous paper different preparation routes for $NiMn_2O_4$ thermistor ceramics have been reported [1]. Semiconductor ceramics $Ni_xMn_{3-x}O_4$ ($x \leq 1$) are known to have applications as highly precise thermistors [2, 3], although spinels based on this system are known to be unstable below 730°C in air. According to the phase diagram [4] $\alpha\text{-}Mn_2O_3$ and $NiMnO_3$ are formed as a result of oxygen contamination.

$$NiMn_2O_4 + \frac{1}{4}O_2 \underset{>730^\circ C}{\overset{<730^\circ C}{\rightleftharpoons}} NiMnO_3 + \frac{1}{2}\alpha\text{-}Mn_2O_3 \qquad (1)$$

At room temperature $NiMn_2O_4$ is in a metastable state. It has been shown that the thermal decomposition of oxalate mixed crystals $NiMn_2(C_2O_4)_3 \cdot 6H_2O$ at 350°–$400^\circ C$ provides a series of defect spinels $Ni_{4/(4+\delta)}Mn_{8/(4+\delta)}\square_{3\delta/(4+\delta)}O_{4.00}$ whose compositions depend on the oxygen partial pressure thus allowing to prepare $NiMn_2O_4$ ($\delta = 0$) at conditions of metastability [5–7]. The compound thus obtained is in a highly dispersed state (about 50 m^2/g). In the range $450^\circ < T < 730^\circ C$ the metastable compound decomposes along to Eq. (1) and above $730^\circ C$ in turn $NiMn_2O_4$ is formed in the equilibrium state.

Moreover, the metastable spinel $Ni_{1.5}Mn_{1.5}O_4$ was found to be accessible following the oxalate route of preparation [7]. Heating above $450^\circ C$ in air leads to the compound $NiMnO_3$ which is stable up to about $770^\circ C$.

$$Ni_{1.5}Mn_{1.5}O_4 + \frac{1}{4}O_2 \xrightarrow{>450^\circ C} \frac{3}{2}NiMnO_3 \qquad (2)$$
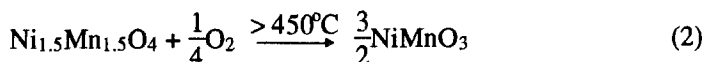
Mg_2TiO_4 as an inverse spinel could be also prepared at metastable conditions provided that homogeneous hydrolysis of a solution of $Ti(OCH_2CH_2OC_2H_5)_4$ and $Mg(OCH_2CH_2OC_2H_5)_2$ in 2-ethoxy-ethanol is carried out followed by evaporation and stepwise heating up to $700^\circ C$ [8, 9]. At increasing temperature Mg_2TiO_4 in the metastable state is intermediately decomposing and only above $1050^\circ C$ the range of stability is attained.

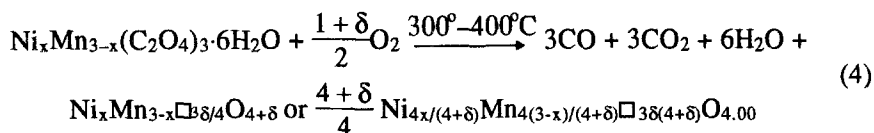$$MgTiO_4 \underset{>1050^\circ C}{\overset{<1050^\circ C}{\rightleftharpoons}} MgTiO_3 + MgO \qquad (3)$$
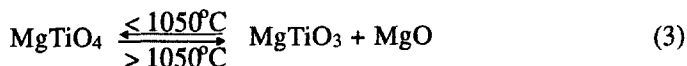
The enthalpies of formation and decomposition of the compounds measured by thermal analysis are the matter of the paper presented. The results are discussed in terms of structural reasons for the occurrence of metastability.

Experimental

Preparation

The preparation of the oxalate mixed crystals $Ni_xMn_{3-x}(C_2O_4)_3 \cdot 6H_2O$ has been already described [5, 6]. Decomposition was shown to be complete at $330^\circ C$ within some hours (6 h applied). The result of decomposition is a defect spinel phase ($0.5 < x < 1.67$)

$$Ni_xMn_{3-x}(C_2O_4)_3 \cdot 6H_2O + \frac{1+\delta}{2}O_2 \xrightarrow{300^\circ - 400^\circ C} 3CO + 3CO_2 + 6H_2O +$$

$$Ni_xMn_{3-x}\square_{3\delta/4}O_{4+\delta} \text{ or } \frac{4+\delta}{4} Ni_{4x/(4+\delta)}Mn_{4(3-x)/(4+\delta)}\square_{3\delta(4+\delta)}O_{4.00} \tag{4}$$

The composition is determined by the molar ratio $Ni/Mn = x/(3-x)$, and δ is a measure of the oxygen contamination. $k = (8-2x+2\delta)/(3-x)$ is the average number of the oxidation state of manganese. At a given x-value δ is varying at constant oxygen partial pressure with temperature and reverse. The assumption that the manganese oxidation state is limited to $k = 4$ leads for $x = 1$ and $0 < \delta < 1$ to the formula $Ni^{II}_{4/5}Mn^{IV}_{8/5} \square_{3/5}O_4$ ($\delta = 1$). For $x = 3/2$ with $0 < \delta < 1/2$ the boundary composition $Ni^{II}_{4/3}Mn^{IV}_{4/3} \square_{1/3}O_4$ is already achieved at $\delta = 1/2$.

Actually, for $x = 1$ at $350^\circ C$ the value $\delta = 0.35$ was found in oxygen and $\delta = 0.19$ in air [5]. Defect free $NiMn_2O_4$ is obtained when the decomposition of $NiMn_2(C_2O_4)_3 \cdot 6H_2O$ mixed crystals is carried out in an atmosphere of reduced oxygen partial pressure (2 vol% O_2/Argon) at $400^\circ C$ (6 h). At these conditions metastable $NiMn_2O_4$ is obtained because reaction (1) is just yet inhibited.

Decomposition of $Ni_{1.5}Mn_{1.5}(C_2O_4)_3 \cdot 6H_2O$ in flowing air at $400^\circ C$ (6 h) permits to prepare the metastable spinel phase $Ni_{1.5}Mn_{1.5}O_4$ [7]. Decomposition to $NiMnO_3$ starts already at $450^\circ C$ along to Eq. (2). However at $450^\circ C$ in air the reaction remains incomplete. Measuring the increase of weight infers that even after 450 h the part of $NiMnO_3$ formed is limited to about 70%. Decomposition of the oxalate mixed crystals at $650^\circ C$ in air (24 h), densification of the powder by pressure (150 MPa) followed by annealing at $700^\circ C$ (50 h) in an oxygen atmosphere, grinding the tablets and twice repeating the procedure lead to the formula $NiMnO_{2.98}$.

Highly dispersed metastable Mg_2TiO_4 (43 m^2/g) is obtained in the result of hydrolysis of mixtures of $Mg(OCH_2CH_2OC_2H_5)_2$ and $Ti(OCH_2CH_2OC_2H_5)_4$ in the molar ratio 2 to 1 in 2-ethoxy-ethanol followed by evaporation and stepwise heating up to $700^\circ C$. The powder has still a small ignition loss of about 1.3%.

Analyses

$NiMn_2O_4$ and $Ni_{1.5}Mn_{1.5}O_4$ both prepared in the metastable state have been analysed by dissolution of the weighing out loss in diluted sulphuric acid containing $VOSO_4$ of defined molarity. The oxidation equivalents localized at the manganese ions are completely transferred to the vanadium species at about $60^\circ C$ without falsification by the presence of air. VO_2^+ ions are formed and the residual concentration of VO^{2+} ions is measured by potentiometric titration manganometrically.

Thermal analysis

A NETZSCH apparatus STA 429 was used for recording TG and DSC traces. For studying the boundary conditions of metastability, $NiMn_2O_4$ and $Ni_{1.5}Mn_{1.5}O_4$ were submitted to thermal cycling with varying heating rates at defined oxygen partial pressure. Measuring of the reaction enthalpies demands calibration. The phase transition of $BaCO_3$ at $T_u = 808°C$ ($\Delta H_u = 17.58$ kJ/mol) recorded with a sensitivity of 0.43 μV/mW (error ≈ 2%) and melting of gold at $T_s = 1069°C$ ($\Delta H_f = 12.60$ kJ·mol^{-1}) recorded with a sensitivity of 0.24 μV/mW (error ≈10%) have been used.

Conductivity measurements

The direct current conductivity of the samples contacted by Ag paste (fired at 800°C, for 1/2 h) was measured between 0° and 70°C utilizing a high resolution digital voltmeter equipped with a constant current source. Details of the apparatus have already been published [10, 11].

Results

Thermoanalytical recording of the decomposition of the spinel compounds for quantitative purposes in the range of metastability fails. Because of kinetic hindrance especially in the final period the reactions along to Eqs (1), (2) or (3) become extremely slow.

$NiMn_2O_4$

Annealing of $NiMn_2O_4$ ceramic samples at 500°C for 100 h in air leads only to a very small degree of decomposition. Analytically the formula $NiMn_2O_{4.01}$ has been found. In the X-ray diffraction diagram the most intense reflexes of $NiMnO_3$ just yet could be observed. On the other hand, at 700° or 350°C changes in structure or composition were not detectable with the aid of chemical analyses or X-ray diffraction after annealing for 100 h. Of course, a maximum rate has to be expected in the range of mean temperatures, because despite of the increasing driving force the kinetics of decomposition is confined the better the lower the temperature is. Conductivity measurements are more sensitive. The data are summarized in Table 1. Commonly, ageing of $NiMn_2O_4$ semiconductor ceramics is restricted to temperatures up to about 150°C. The drift of the data observed in this range is reduced to values below 0.1% during a period of about 200 h. In the frame of such small alterations the electrical data remain unchanged during annealing at 250°C. However, at 350°C significantly enlarged fluctuations arise.

Table 1 Conductivity data of $NiMn_2O_4$ ceramics in dependence on the annealing temperature ($po_2 = 0.21 \cdot 10^5$ Pa)

Sample	150°C, 1610 h		250°C, 100 h		350°C, 90 h	
	$\Omega^{-1}cm^{-1}$	B/K	$\Omega^{-1}cm^{-1}$	B/K	$\Omega^{-1}cm^{-1}$	B/K
1	$3.2 \cdot 10^{-4}$	3807	$3.3 \cdot 10^{-4}$	3797	$1.3 \cdot 10^{-4}$	3956
2	$2.6 \cdot 10^{-4}$	3811	$2.7 \cdot 10^{-4}$	3803	$1.1 \cdot 10^{-4}$	3896
3	$3.7 \cdot 10^{-4}$	3805	$3.7 \cdot 10^{-4}$	3801	$2.5 \cdot 10^{-4}$	3839
4	$2.7 \cdot 10^{-4}$	3798	$2.8 \cdot 10^{-4}$	3799	$1.4 \cdot 10^{-4}$	3909
5	$3.9 \cdot 10^{-4}$	3803	$3.9 \cdot 10^{-4}$	3793	$2.6 \cdot 10^{-4}$	3851
	$(3.2\pm0.5)\cdot 10^{-4}$	3805±5	$(3.3\pm0.6)\cdot 10^{-4}$	3799±5	$(1.8\pm0.7)\cdot 10^{-4}$	3890±48

Table 2 Increase of weight Δm and of the parameter p of $NiMn_2^{3+}{}_{2p}O_{4+p}$ powders freshly ground from ceramics

Temp./ °C	Δm / %			p			Phases observed[*]		
	10 h	50 h	100 h	10 h	50 h	100 h	10 h	50 h	100 h
700	0	0	0	–	–	0.01	–	–	sp./il.
600	0.3	0.6	0.7	0.01	0.07	0.07	sp./il.	sp./il.	–
500	2.1	2.4	2.7	0.27	0.33	0.39	sp./il.	–	–
350	0.1	0.1	0.3	0.00	0.01	0.04	sp.	sp.	sp./il.

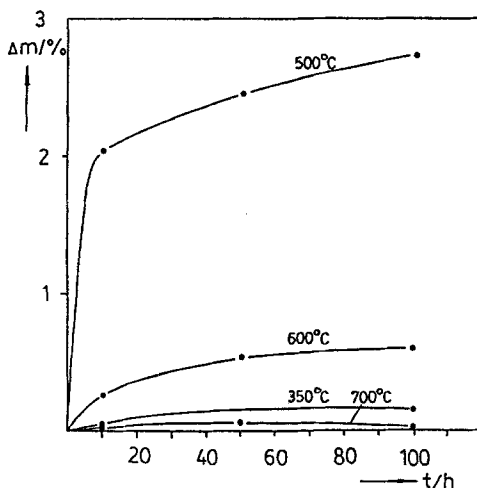The electrical properties of the samples become spread showing among one another extended deviations.

Fig. 1 Increase of weight Δm of NiMn$_2$O$_4$ powders ground along to Eq. (1) during annealing at different temperatures

On the other hand, NiMn$_2$O$_4$ powders resulting from grinding of the ceramics (15 min in an achate vibrating mill) exhibit a very much higher reactivity in the decomposition process along to Eq. (1). These results are collected in Table 2. According to the general formula NiMn$_2^{3+p}$O$_{4+p}$ the increase of weight is the result of oxidation of manganese (Eq. (1)). Complete oxidation is achieved at Δm = 3.44% or $p = 0.5$, respectively. The values p have been separately determined by oxidimetric analyses. At 500°C the decomposition shows a maximum reaction rate, which is demonstrated in Fig. 1. At 700°C the driving force is still comparatively low and at 350°C the decomposition is already blocked by kinetic reasons.

Table 3 Cancelling of the metastability of the fired NiMn$_2$O$_4$ powder by milling proved by annealing at 500°C (100 h)

Sample	(1)	(2)	(3)	(4)	(5)
	Ceramics	Ceramics powdered (15 min)	Powder heated 1000°C (4 h) 800°C (20 h)	Powder as sample (3) milled 1 h	Powder as sample (3) 5 min mortar powd.
$m\%$	0.1	2.7	0	3.1	1.3

Extending the annealing studies at 500°C to $NiMn_2O_4$ powders which were fired as above the ceramics at 1000°C (4 h) followed by annealing at 800°C (20 h), leads again to a vanishing reactivity. Following the analytical data and X-ray diffraction the decomposition fails entirely (Table 3). Only after grinding reaction (1) takes place within the annealing time applied.
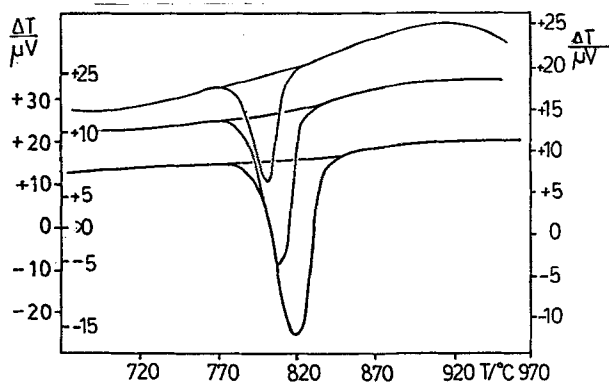

Fig. 2 DSC plot of $NiMnO_3/1/2\alpha-Mn_2O_3$ mixtures resulting from annealing of $NiMn_2O_4$ powder at 500°C formed in the metastable state on the oxalate decomposition route: 42.89 mg, 10 $deg\cdot min^{-1}$ 63.6 $kJ\cdot mol^{-1}$ (—); 42.89 mg, 5 $deg\cdot min^{-1}$ 59.1 $kJ\cdot mol^{-1}$ (—): 32.82 mg, 2.5 $deg\cdot min^{-1}$ 59.9 $kJ\cdot mol^{-1}$ (—)

Even the highly dispersed form of unstable $NiMn_2O_4$ powders prepared by low temperature decomposition of the oxalate mixed crystals in air needs at 500°C approximately 20 h for complete decomposition.

Therefore, measurements of the enthalpy of formation of $NiMn_2O_4$ in turn of Eq. (1) had to start from the mixture of $NiMnO_3$ and $1/2Mn_2O_3$ obtained by annealing of ground $NiMn_2O_4$ ceramics or of $NiMn_2O_4$ powder prepared as a metastable phase on the oxalate route, respectively. 500°C were applied for annealing thus forming an intimite mixture of $NiMnO_3$ and $\alpha-Mn_2O_3$.

Figures 2 and 3 show the DSC plots of the return of reaction (1) for the two mixtures resulting from the different $NiMn_2O_4$ sources at an oxygen partial pressure $p_{O_2} = 2.1\cdot10^{+4}$ Pa. The mean values 60.9 and 60.3 $kJ\cdot mol^{-1}$ are found, i.e. there is no significant difference between the two mixtures. The enthalpy of the reaction is given by the value 61 $kJ\cdot mol^{-1}$ (10% error).

$Ni_{1.5}Mn_{1.5}O_4$

The metastable spinel $Ni_{1.5}Mn_{1.5}O_4$ prepared by oxalate mixed crystal decomposition in flowing air at 400°C (6 h) was found to be cubic with a lattice constant $a_0 = 835.1(5)$ pm. At lower temperature, e.g. at 350°C, a defect spinel

with an increased Mn^{IV} content has been obtained:
$Ni_{1.47}Mn^{III}_{0.81}Mn^{IV}_{0.66}\square_{0.06}O_{4.00}$ [5]. The metastable compound has to be interpreted
as an end member of the series $Ni_{1.5}Mn_{1.5}\square_{3\delta/4}O_{4+\delta}$ ($\delta = 0$).

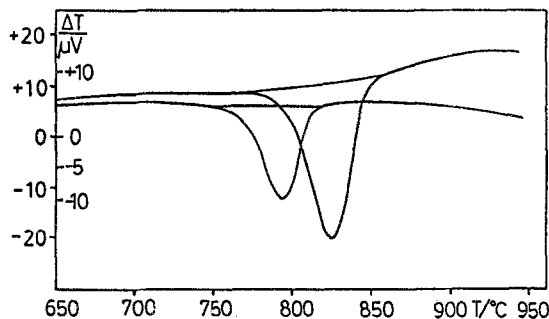Fig. 3 DSC plot of $NiMnO_3/1/2\alpha$-Mn_2O_3 mixtures resulting from annealing of ground $NiMn_2O_4$
      ceramics at 500°C: 42.16 mg, 10 deg·min^{-1}, 61 kJ·mol^{-1} (—); 41.44 mg, 5 deg·min^{-1},
      58.4 kJ·mol^{-1} (—)

The formula $Ni^{II}(Ni^{II}_{0.5}Mn^{IV}_{0.5}(Mn^{III})O_4(Mn^{III})O_4$ appears to be unlikely because
of the well-known high degree of inversion for $NiMn_2O_4$, which implies the for-
mation of Mn^{II} on the A and Mn^{IV} on the B sites of the spinel structure. Because
of the low decomposition temperature the random distribution of cations in the
oxalate mixed crystals is assumed to be widely maintained in the defect spinel
precursor. Therefore, the formula

$$Ni^{II}_{1-y}Mn^{III}_{y-p}Mn^{II}_p \ (Ni^{II}_{0.5+y}Mn^{IV}_{0.5+p}Mn^{III}_{1-y-p})O_4 \qquad (4)$$

with $y \approx 0.5$ and $y \approx p$ seems to be probable.

The metastable compound $Ni_{1.5}Mn_{1.5}O_4$ was suggested to be a suitable precur-
sor for the formation of $NiMnO_3$. On the other hand, the entropically unfavoured
formation of the well-defined ordering of the cations occupying the octahedral
sites of the ilmenite type structure requires sufficient mobility of the Ni^{II} and
Mn^{IV} cations. Analyses provide the composition $NiMnO_{2.98}$ for the powder result-
ing from decomposition of $Ni_{1.5}Mn_{1.5}(C_2O_4)_3$ 6H$_2$O mixed crystals at 650°C in
air. No foreign reflexes have been observed in the X-ray diffraction pattern. Hold-
ing of $Ni_{1.5}Mn_{1.5}O_4$ at 730°C in air (100 h) leads also to incomplete $NiMnO_3$ for-
mation. Obviously, because of kinetic reasons it is difficult to prepare $NiMnO_3$ in
a homogeneous single-phase state along to Eq. (3). Already above 70°C $NiMnO_3$
decomposes

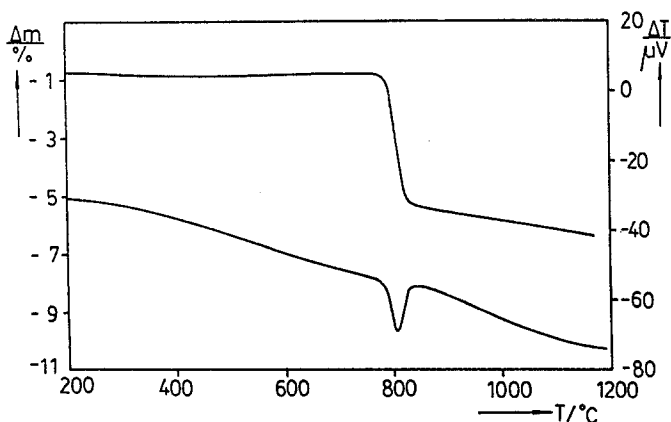$$NiMnO_3 \rightarrow c \ NiO + \frac{(2-c)}{3} Ni_{(3-3c)/(2-c)}Mn_{3/(2-c)}O_4 + \frac{(1+c)}{6} O_2 \qquad (5)$$
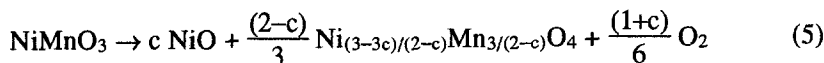
Fig. 4 Thermal decomposition of $NiMnO_{2.98}$ along to Eq. (5), $c = 0.387$

Figure 4 shows the results of thermoanalysis. NiO and the spinel $Ni_{1.14}Mn_{1.86}O_{4.00}$ are formed ($c = 0.387$). The loss of weight of 4.6% expected according to Eq. (5) was accurately observed by thermogravimetric measurements. The enthalpy of the reaction has been measured with different heating rates at an oxygen partial pressure $p_{O_2} = 212$ mbar providing the values $48.2\ kJ \cdot mol^{-1}$ (10 deg·min^{-1}) $48.3\ kJ \cdot mol^{-1}$ (5 deg·min^{-1}) and $47.1\ kJ \cdot mol^{-1}$ (2.5 deg·min^{-1}) which leads to the mean value of $48\ kJ \cdot mol^{-1}$ (error 10%).

Deduced from these results and in accordance with the phase diagram [4] the observation of $Ni_{1.5}Mn_{1.5}O_4$ formation at 800°C, which has been reported in the literature [12] as a result of the decomposition of $NiMnO_2(OH)$, appears to be unlikely.

Indeed, the pathway for the preparation of $NiMnO_3$ seems to be widely blocked up. By hydrothermal synthesis starting from NiO and MnO_2 the compound has been also obtained only as a component of a mixture [13].

Mg₂TiO₄

The inverse spinel formed in the metastable state provides the DSC plot shown in Fig. 5. Two distinct exothermic peaks with the on-set temperature $T_1 = 760°C$ ($\Delta H_1 = -2.9 \pm 0.5\ kJ \cdot mol^{-1}$) and $T_2 = 960°C$ ($\Delta H_2 = -4.8 \pm 0.6\ kJ \cdot mol^{-1}$) are observed (curve *a*) indicating the decomposition along to Eq. (3), which is followed by the formation of Mg_2TiO_4 at $T_3 = 1130°C$ ($\Delta H_3 = 8.0 \pm 8\ kJ \cdot mol^{-1}$). Heating of a sample, which had been quenched after heating up to the first peak (curve *b*), provides only the second peak (curve *c*) and again heating leads to curve (*d*) of Fig. 5 showing only the enthalpy of the formation of Mg_2TiO_4 in turn of Eq. (3). MgO, $MgTiO_3$ and residual Mg_2TiO_4 are found in the range of the first

and second exothermic peak in the X-ray diffraction diagram. In accordance with expectation the sum of the two exothermic enthalpies corresponds approximately to the endothermic enthalpy of Mg_2TiO_4 formation. Presumably MgO nucleation and growth goes ahead before $MgTiO_3$ initially remaining partially dissolved in the spinel phase starts to separate. However, as shown in Table 4, the lower the heating rate is the more the second peak prevails indicating that $MgTiO_3$ and MgO are formed in close relation as a result of decomposition of Mg_2TiO_4 in the range of metastability.

Complete decomposition is achieved after annealing at 900°C (4 h) or annealing at 1050°C (3 h). Obviously, the temperature where the free enthalpy of the formation of Mg_2TiO_4 becomes negative is above 1050°C. In the literature a value of 1000°C has been estimated as the lowest limit for Mg_2TiO_4 formation [14]. For the reaction enthalpy a value of 19.3 ± 1.6 kJ·min^{-1} at 1190°C was measured by DSC. This value is confirmed by extrapolation of the values of Table 4 to a heating rate of $q = 0$.

Table 4 Dependence of metastable Mg_2TiO_4 decomposition behaviour on the heating regime at T_{ON} (1) and T_{ON} (2) and formation of Mg_2TiO_4 at T_{ON} (3)

Heating rate /	Peak 1		Peak 2		Peak 3	
deg·min^{-1}	$T_{ON}(1)/°C$	ΔH /kJ·mol^{-1}	$T_{ON}(2)/°C$	ΔH /kJ·mol^{-1}	$T_{ON}(3)/°C$	ΔH /k·mol^{-1}
20	780	-2.6 ± 0.3	970	-2.2 ± 0.1	1120	$+4.8 \pm 0.6$
10	760	-2.4 ± 0.2	960	-4.8 ± 0.6	1130	$+8.0 \pm 0.8$
5	750	-1.6 ± 0.5	910	-8.8 ± 0.8	1150	$+11.2 \pm 1.0$
3	–	–	880	-16.7 ± 1.6	1160	$+16.7 \pm 1.6$

Wechsler and Navrotzky [14] measured a value of 16.9 ± 2.2 kJ·mol^{-1} at 700°C by dissolution calorimetry. Extrapolation to 920°C leads to 20.8 kJ·mol^{-1} which is in sufficient agreement with the data observed in this paper.

Discussion

Obviously, homogeneity and isotropy of the highly disturbed transition state resulting from thermal decomposition of the oxalate mixed crystals $Ni_xMn_{3-x}(C_2O_4)_3 \cdot 6H_2O$ at comparatively low temperatures involves suitable prerequisites for an ordering of the oxygen ions to cubic dense packing. The cations are assumed to occupy the vacancies arranging their preferred configurations (coordination numbers) in close relation with oxygen ion ordering. Considering a stepwise decrease of the entropy the cubic structure seems to be the next neigh- boured suitable stage from the strongly disordered transition state

which is most easily achieved from oxalate decomposition thus leading to the formation of a spinel phase at metastable conditions. It is even possible to alter the vacancy concentration in small limits in dependence on oxygen partial pressure and temperature without cancelling the metastable state. Using such a pathway the quasi defect free metastable compounds $NiMn_2O_4$ and $Ni_{1.5}Mn_{1.5}O_4$ could be prepared.

In such a context the formation of the inverse spinel Mg_2TiO_4 at metastable conditions as a result of homogeneous hydrolysis of $Ti(OCH_2CH_2OC_2H_5)_4$ and $Mg(OCH_2CH_2OC_2H_5)_2$ in 2-ethoxyethanol followed by evaporation and stepwise calcination up to 700°C appears to be understandable, too [8, 9]. γ-Fe_2O_3 is formed as a metastable compound during careful oxidation of Fe_3O_4 even at 180°C [15]. Of course, topotaxy achieves importance in solid state reactions the better the lower the reaction temperature is. Thermal dehydration of $MgWO_4 \cdot 2H_2O$ leads in two distinct topotactic steps at 100° and 150°C to multiply twinned $MgWO_4$, reported to exist above 1200°C only [16].
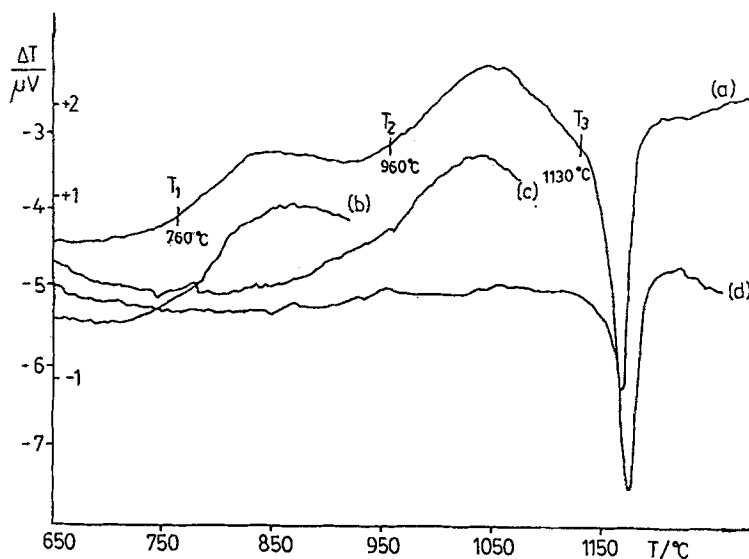

Fig. 5 DSC plot of decomposition of metastable Mg_2TiO_4 and formation along to Eq. (3) on heating with 10 deg·min^{-1} (a) and stepwise heating up to 960°C (b) followed by heating up to 1130°C (c) followed by heating up to 1200°C (d)

The metastability of the inverse spinel type compounds $NiMn_2O_4$, $Ni_{1.5}Mn_{1.5}O_4$ and Mg_2TiO_4 accessible on the preparation routes reported are suggested to result from both, random distribution of different cations on the different crystallographic sites in the spinel lattice, and the entropically unfavoured step of cation ordering, needed for the nucleation and growth of ilmenite type

crystals of $NiMnO_3$ along to Eqs (1) and (2) or according to Eq. (3) for $MgTiO_3$, respectively.

However, the decomposition reactions leading to $NiMnO_3$ seem to be significantly more inhibited because of the kinetic indolence of the Mn^{IV} ions (d^3 electron configuration). $MgTiO_3$ and MgO seem to be easier formed as a result of decomposition of Mg_2TiO_4 than $NiMnO_3$ from $Ni_{1.5}Mn_{1.5}O_4$ or from $NiMn_2O_4$, respectively.

The thermodynamic data infer that random distribution of Mg^{II} and Ti^{IV} on the B sites of the inverse spinel structure cause stabilization by the entropy term in the range of higher temperature. Mg_2TiO_4 formation in turn of Eq. (3) is coupled with an endothermic enthalpy effect of comparatively small size: $+19.3\pm1.6$ $kJ\cdot mol^{-1}$. Therefore, the driving force is assumed to attain above $1050°C$ only a small value. However, despite of the small negative free enthalpy the formation of Mg_2TiO_4 from the intimite $MgO/MgTiO_3$ mixture is comparatively soon finished.

Presumably, the formation of $NiMn_2O_4$ in turn of Eq. (1) from the intimite $NiMnO_3/1/2\alpha$-Mn_2O_3 mixture leading to an increased endothermic enthalpy effect of 61 $kJ\cdot mol^{-1}$ above $730°C$ is also supported by the random distribution of cations on the different crystallographic sites (formula 4).

Additionally, oxygen release is suggested to give rise for a negative free enthalpy sufficiently high for enhancement of the reaction rate of $NiMn_2O_4$ formation. In reverse, the decomposition reaction is strongly inhibited.

References

1 A. Feltz, J. Töpfer and F. Schirrmeister, J. Europ. Ceram. Soc., 9 (1992) 187.
2 H. Walch, Siemens-Zeitschr., 47 (1973) 66.
3 S. K. Sakkar, M. L. Sharma, H. L. Bhaskar, K. C. Nagpal, J. Mater. Sci., 19 (1984) 545.
4 D. C. Wickham, J. Inorg. Nucl. Chem., 26 (1964) 1369.
5 A. Feltz and J. Töpfer, Z. Anorg. Allg. Chem., 576 (1989) 71.
6 X.-X. Tang, A. Manthiram and J. B. Goodenough, J. Less-Comm. Metals, 156 (1989) 357.
7 A. Feltz, J. Töpfer and U. Richter, Europ. J. Solid State Inorg. Chem., in press.
8 A. Feltz and F. Schmidt, Z. Chem., 27 (1987) 414.
9 F. Schmidt and A. Feltz, Z. Anorg. Allg. Chem., 573 (1989) 208.
10 F. Schirrmeister and A. Blayer, Hermsd. Techn. Mitt., 30 (1990) 2570.
11 F. Schirrmeister and A. Feltz, Exp. Techn. Physik, in press.
12 N. Yamamoto, J. Japan. Soc. Powder and Powder Metal, 33 (1986) 48.
13 T. J. Swoboda, R. C. Toole and J. D. Vangham, J. Phys. Chem. Solids, 5 (1958) 293.
14 B. A. Wechsler and A. Navrotsky, J. Solid State Chem., 55 (1984) 165.
15 A. Rousset, G. Boissier, J. B. Caffin and F. Chassagneux, C. R. Acad. Sci. Serie II, 12 (1984) 781.
16 J. R. Günter and E. Dubler, J. Solid State Chem., 65 (1986) 118.

Zusammenfassung — Ausgehend von $Ni_xMn_{3-x}(C_2O_4)_36H_2O$ Oxalatmischkristallen führt die thermische Zersetzung bei vermindertem partialem Druck von Sauerstoff ($po_2 = 2 \%$) zur Bildung von $NiMn_2O_4$ (x=1) unter metastabilen Bedingungen. Das nur in metastabilem Zustand exis-

tierende $Ni_{1.5}Mn_{1.5}O_4$ ($x=1.5$) wurde ebenfalls hergestellt. Beide Spinellverbindungen sind vom stark umgekehrten Typ. Über einen Sol-Gel Herstellungsweg wurde gefunden, daß Mg_2TiO_4 ebenfalls in metastabilem Zustand gebildet wird. Tempern ergibt eine Zersetzung der Verbindungen, was zu $NiMnO_3$ und $1/2Mn_2O_3$ oder nur $NiMnO_3$ oder $MgTiO_3$ und MgO führt. Die Reaktionsgeschwindigkeiten sind für die Zersetzung von $NiMn_2O_4$ und $Ni_{1.5}Mn_{1.5}O_4$ niedriger als für die von Mg_2TiO_4. Die Rückreaktion der Bildung von $NiMn_2O_4$ oberhalb 730°C zeigt eine endotherme Enthalpie von +61 kJ·mol^{-1}. Für die Bildung von Mg_2TiO_4 oberhalb 1050°C wurde eine endotherme Enthalpie von +19.3 kJ·mol^{-1} gefunden. Die Ergebnisse wurden unter Berücksichtigung der Struktureigenschaften der Oxide diskutiert.