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Thermal decomposition of mixed crystals $Ni_xMn_{3-x}(C_2O_4)_3 \cdot 6H_2O$

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Abstract

The preparation and properties of the mixed crystal series $Ni_xMn_{3-x}(C_2O_4)_3 \cdot 6H_2O$ are described. The thermal decomposition of these compounds was observed by thermal analysis. The decomposition products of the compositions with $0.5 < x < 2$ in the range 350–400°C are defect spinel phases $Ni_xMn_{3-x}\square_{3\delta/4}O_{4+\delta}$. The composition of the products is discussed in relation to dependence on temperature and oxygen pressure.

INTRODUCTION

Compounds with spinel structure in the system $Ni_xMn_{3-x}O_4$ are of interest in connection with thermistor ceramics. It has already been shown that their preparation via the thermal decomposition of oxalate mixed crystals $Ni_xMn_{3-x}(C_2O_4)_3 \cdot 6H_2O$ is advantageous [1]. A report has also appeared on the primarily formed decomposition products and their properties. At temperatures of 350–400°C metastable spinels with cation vacancies $Ni_xMn_{3-x}\square_{3\delta/4}O_{4+\delta}$ are formed in a wide composition range [2,3]. The thermodynamically stable phases $NiMnO_3$ and α-Mn_2O_3 are formed with increasing temperature in agreement with the phase diagram of the system NiO–Mn_2O_3–O_2 [4]. The concentration of cation vacancies is temperature dependent. This has been shown for the series $NiMn_2\square_{3\delta/4}O_{4+\delta}$ [5].

The thermal decomposition of oxalates has been investigated by several authors; a review was given by Dollimore [6]. However, there is no information in the literature about the properties of the mixed crystals $Ni_xMn_{3-x}(C_2O_4)_3 \cdot 6H_2O$ and their thermal decomposition. The decomposition of the substances $MnC_2O_4 \cdot 2H_2O$ and $NiC_2O_4 \cdot 2H_2O$ has already been investigated, but there are conflicting data about the products formed

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by the thermal decomposition of $MnC_2O_4 \cdot 2H_2O$. Dollimore et al. [7] found Mn_3O_4 to be the reaction product of the thermal decomposition in air. Macklen [8] described a poorly crystallized product which changes into α-Mn_2O_3 at 400°C. The thermal decomposition of $NiC_2O_4 \cdot 2H_2O$ leads to NiO but different values have been reported for the temperature of decomposition. Wiedemann and Nehring [9] reported a value of 330°C whereas Doremieux and Boulle [10] found 290°C.

In this article we describe the mixed crystal series $Ni_xMn_{3-x}(C_2O_4)_3 \cdot 6H_2O$ and the thermal decomposition of selected compositions using thermal analysis.

MATERIALS AND METHODS

Samples of the series $Ni_xMn_{3-x}(C_2O_4)_3 \cdot 6H_2O$ were prepared by adding oxalic acid to a solution of $MnCO_3$ and $NiCO_3$ (reagent grade) in acetic acid. An excess of oxalic acid was used to reduce the amount of higher valent manganese in $MnCO_3$. To obtain a precipitate with exact composition it was dried in a vacuum rotation evaporator at 50°C. The contents of nickel, manganese and oxalate were determined by chemical analysis.

X-ray diffraction investigations were carried out with an HZG4 goniometer using Cu Kα radiation filtered with Ni. Thermal analysis was carried out with the simultaneous TG–DTA system STA 429 (Netsch). The measurements were carried out with a heating rate of 5 K min^{-1} in different atmospheres. The sample weight was about 15 mg and we used shallow corundum crucibles. Experiments with higher sample weights (80 mg) in deep crucibles led to a delay of decomposition and the end of decomposition was found to be at temperatures higher by about 60 K. This is due to the depression of oxalate decomposition by a local atmosphere rich in the decomposition products water and carbon oxides. The oxidation state of the decomposition products was estimated by a redox titration. The samples were dissolved in a sulphuric acid solution of VO^{2+} ions and the excess VO^{2+} was titrated with $KMnO_4$. In one case the degree of oxidation was controlled by a solid state coulometric titration with the analysis system OXYLYT (developed at Kernforschungszentrum Rossendorf, Germany).

RESULTS AND DISCUSSION

The compositions of the precipitation products as determined by chemical analysis are listed in Table 1. Substances were obtained and investigated that had the reported water contents. X-ray investigation of the oxalates showed the formation of mixed crystals in the whole composition range. Deyrieux et al. [11] found that the substances $MnC_2O_4 \cdot 2H_2O$ and $NiC_2O_4 \cdot 2H_2O$ crystallized in the monoclinic system in space group C_{2c}. All the prepared mixed crystals were also identified as monoclinic. The

TABLE 1

Composition and lattice parameters of compounds of the series $Ni_xMn_{3-x}(C_2O_4)_3 \cdot 6H_2O$

x	Composition	$a_0 \pm 5$ (pm)	$b_0 \pm 5$ (pm)	$c_0 \pm 5$ (pm)	$\beta \pm 0.4$ (°)
0	$MnC_2O_4 \cdot 2H_2O$	1199	560	999	128.1
0.50	$Ni_{0.50}Mn_{2.50}(C_2O_4)_3 \cdot 6.0H_2O$	1209	562	990	128.4
1.00	$Ni_{1.00}Mn_{2.00}(C_2O_4)_3 \cdot 6.5H_2O$	1206	554	987	128.0
1.33	$Ni_{1.33}Mn_{1.67}(C_2O_4)_3 \cdot 6.9H_2O$	1210	556	991	128.5
1.50	$Ni_{1.50}Mn_{1.50}(C_2O_4)_3 \cdot 7.0H_2O$	1201	551	984	128.3
1.67	$Ni_{1.67}Mn_{1.33}(C_2O_4)_3 \cdot 6.9H_2O$	1207	547	986	128.3
2.00	$Ni_{2.00}Mn_{1.00}(C_2O_4)_3 \cdot 6.5H_2O$	1199	543	983	128.3
2.57	$Ni_{2.57}Mn_{0.43}(C_2O_4)_3 \cdot 6.8H_2O$	1194	539	982	128.6
3	$NiC_2O_4 \cdot 2.4H_2O$	1185	529	977	127.1

lattice constants are shown in Table 1 and their dependence on composition is shown in Fig. 1. A trend of decreasing lattice parameters with increasing composition parameter x can be observed, caused by the smaller ionic radius of the Ni^{2+} ion in comparison with the Mn^{2+} ion.

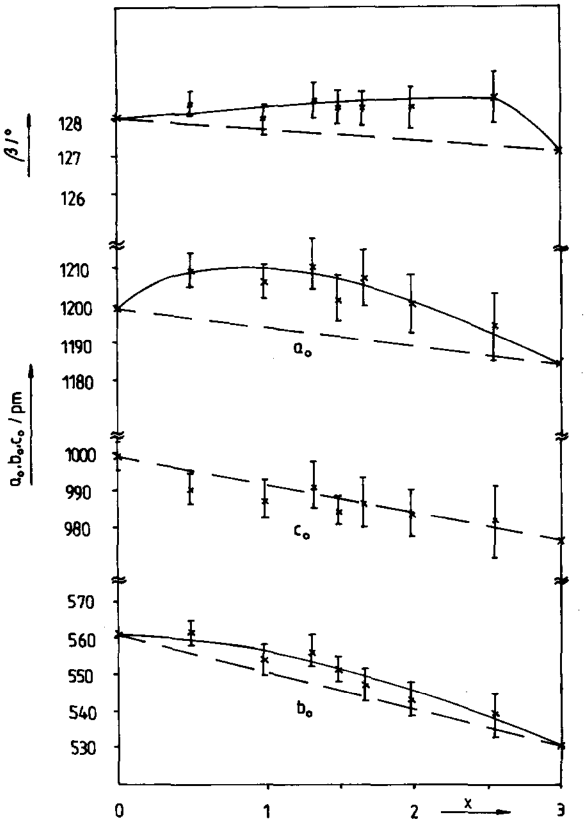


Fig. 1. Lattice parameters of compounds of the series $Ni_xMn_{3-x}(C_2O_4)_3 \cdot (6+n)H_2O$ in dependence on composition.

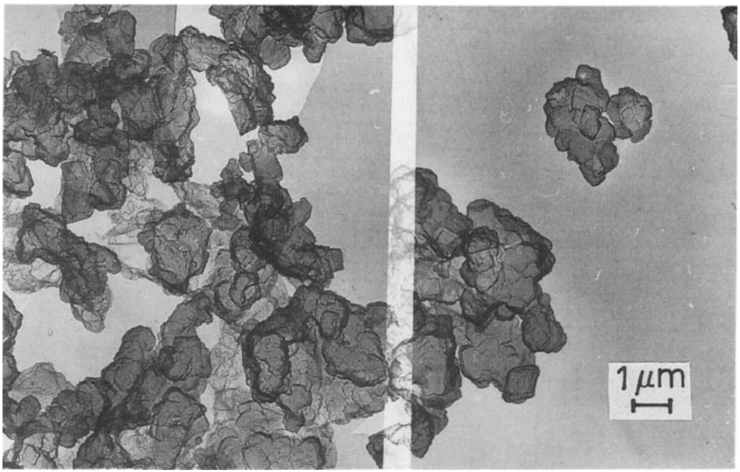


Fig. 2. TEM micrograph of $NiMn_2(C_2O_4)_3 \cdot 6.5H_2O$.

The oxalate particles are strongly aggregated. Figure 2 shows a transmission electron (TEM) micrograph of the compound $NiMn_2(C_2O_4)_3 \cdot 6.5H_2O$. The particles are 1–5 μm in diameter. A d_{50} value of 4 μm was measured by sedimentation analysis of a suspension in *n*-butanol.

The thermal decomposition of $MnC_2O_4 \cdot 2H_2O$ is a two-stage process (Fig. 3). In a first stage beginning at 110°C water is removed, as observable from an endothermic peak in the DTA signal. Already at 130°C the expected mass loss of 20% has been reached. The exothermic decomposition of the oxalate begins at 230°C and is complete at 300°C. A further

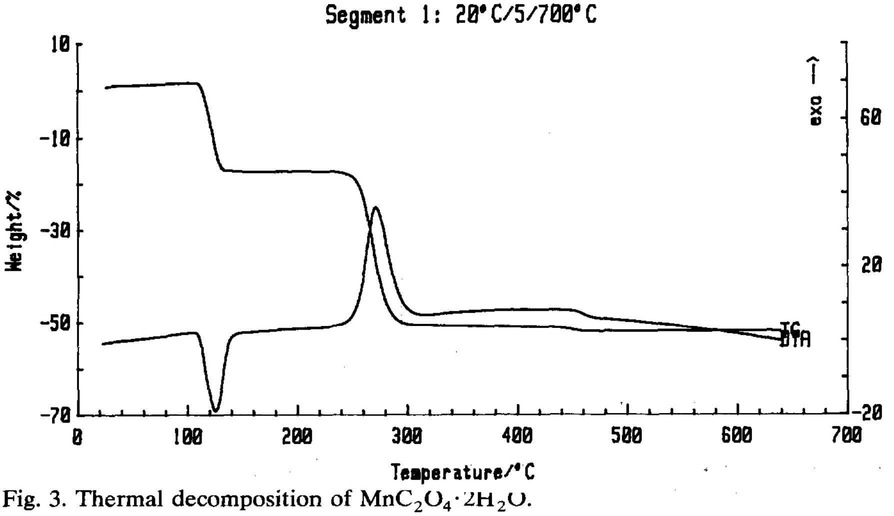


Fig. 3. Thermal decomposition of $MnC_2O_4 \cdot 2H_2O$.

TABLE 2

Reaction products of the thermal decomposition of $Ni_xMn_{3-x}(C_2O_4)_3\cdot 6H_2O$ in air

x	Conditions	Reaction product	δ	Δm (%)	
				exp	calc
0	6 h, 350°C	$MnO_{1.54}$	–	53.9	55.5
0.50	6 h, 350°C	$Ni_{0.47}Mn_{2.34}\square_{0.19}O_4$	0.27	54.8	55.9
1.00	6 h, 350°C	$Ni_{0.95}Mn_{1.91}\square_{0.14}O_4$	0.19	56.4	57.1
1.33	6 h, 350°C	$Ni_{1.29}Mn_{1.61}\square_{0.11}O_4$	0.15	56.4	57.8
1.50	6 h, 350°C	$Ni_{1.47}Mn_{1.47}\square_{0.06}O_4$	0.09	56.2	57.9
1.67	6 h, 350°C	$Ni_{1.66}Mn_{1.32}\square_{0.01}O_4$	0.02	56.6	57.8
2.00	6 h, 350°C	$Ni_{2.00}Mn_{1.00}O_{3.82}$	−0.18	57.4	58.8
3.00	6 h, 350°C	NiO	–	60.7	60.7

mass loss of 1% occurs at 450°C. The composition of a sample obtained by thermal decomposition of manganese oxalate during 6 h. at 350°C was $MnO_{1.54}$ (Table 2). The average oxidation state of manganese is thus equal to 3.08. The sample did not show sharp X-ray reflections, and an exact identification of the crystal structure was not possible. The difference between the expected and the observed (6 h, 350°C) mass loss Δm, which is also shown in Table 2, is remarkable.

For all manganese-containing substances the measured mass loss was slightly lower than that expected. To prove the completeness of decomposition the 350°C product was investigated by IRS, and no indication of the existence of oxalate was found. We assume that the surface active amorphous manganese oxide had adsorbed atmospheric substances such as water or CO_2. The actual carbon and hydrogen contents were found by C/H analysis. The composition of the product was calculated using the manganese content (determined by heating to Mn_3O_4) and the values from the C/H determination (about 0.5% with an absolute error of 50%). Taking account of the error in the C and H contents, the calculated composition is in the range $MnO_{1.30-1.55}(CO_2)_{0.01-0.05}(H_2O)_{0.20-0.30}$. To confirm the composition of the substance the average oxidation state of manganese was independently determined by a solid state coulometric titration. The sample was heated to Mn_3O_4 and the released oxygen was measured electrochemically [12]. A value of 3.076 ± 0.002 was found for the average oxidation state and we therefore concluded that the decomposition product of manganese oxalate at 350°C has the formula $MnO_{1.54}(CO_2)_{0.01}(H_2O)_{0.20}$. With further increase of temperature the adsorbates are desorbed and at about 500°C α-Mn_2O_3 is produced.

The thermal decomposition of nickel oxalate is also a two stage process (Fig. 4). Starting from $NiC_2O_4\cdot 2.4H_2O$, up to 160°C water is separated and the mass loss of 3.8% corresponds to the formation of the oxalate with two moles of water. Further removal of water starts at 160°C, accompanied

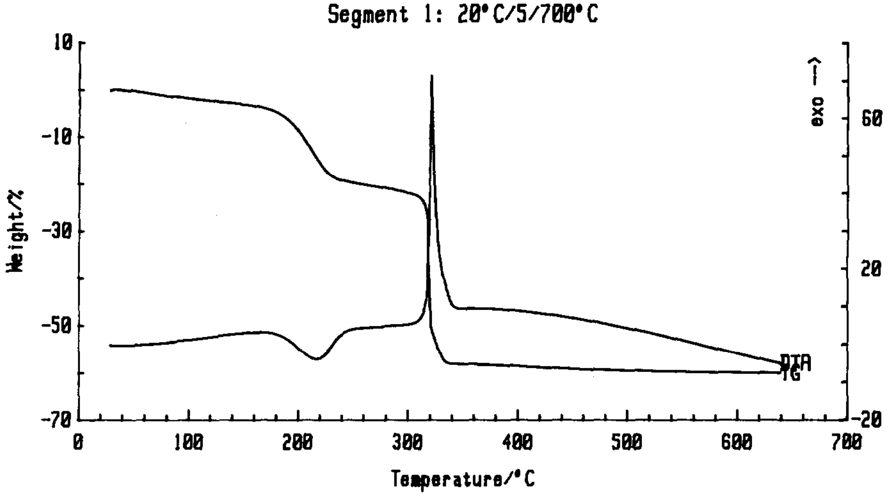


Fig. 4. Thermal decomposition of $NiC_2O_4 \cdot 2.4H_2O$.

by an endothermic DTA signal, and is complete at 250°C. Afterwards the exothermic decomposition of the oxalate proceeds; this ends at 340°C. The reaction product is NiO and the expected mass loss of 60.7% is reached.

Thermal decomposition of the mixed crystals

The compound $Ni_xMn_{3-x}(C_2O_4)_3 \cdot 6H_2O$ was also studied by thermal analysis. Because all compositions showed similar thermal behaviour the results are discussed for the example $NiMn_2(C_2O_4)_3 \cdot 6.5H_2O$ (Fig. 5). The

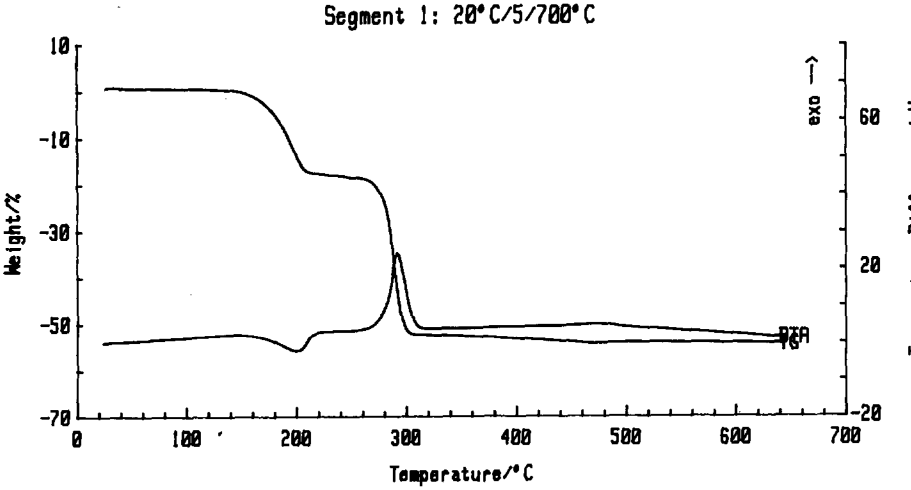


Fig. 5. Thermal decomposition of $NiMn_2(C_2O_4)_3 \cdot 6.5H_2O$.

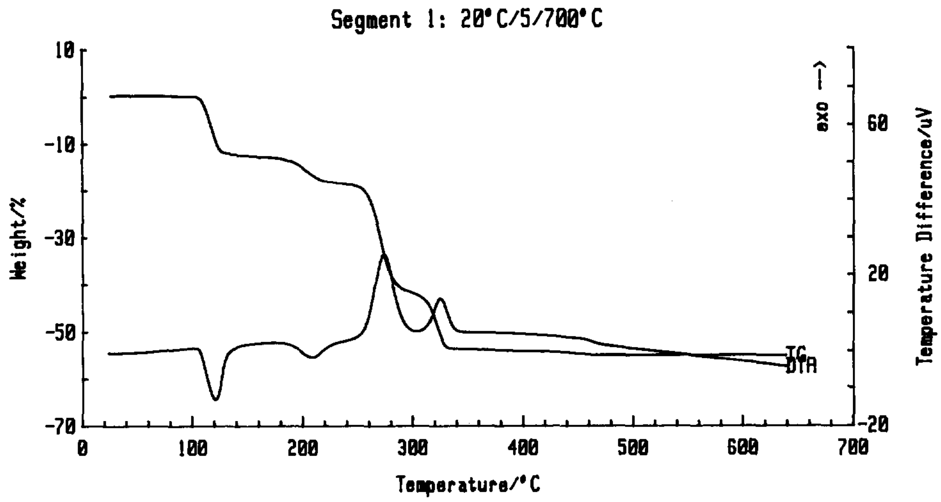


Fig. 6. Thermal decomposition of a mixture of $NiC_2O_4 \cdot 2.4H_2O$ and $2MnC_2O_4 \cdot 2H_2O$.

first stage corresponding to the separation of water starts at 140°C and is finished at 220°C, accompanied by an endothermic DTA peak. The subsequent decomposition of the oxalate ends at 310°C. Simultaneously an exothermic DTA peak occurs. A sample of $NiMn_2(C_2O_4)_3 \cdot 6.5H_2O$ which was heated for 6 h at 350°C showed the reflections of a cubic spinel. The composition was determined to be $NiMn_2O_{4.19}$, which means that the spinel contains cation vacancies. The spinel also adsorbed water and carbon dioxide. The contents of hydrogen and carbon were 0.5% and 0.2% respectively. Heating the samples in a vacuum up to 200°C led to the removal of the adsorbates. A mass loss of 1.3% was detected without any change in the oxidation state of the sample. The process is reversible: the mass increases again on exposing the sample to air.

The homogeneous distribution of the cations in the lattice of the oxalates is a prior assumption for the formation of defect spinels. A mixture of $NiC_2O_4 \cdot 2.4H_2O$ and $2MnC_2O_4 \cdot 2H_2O$ was heated to 350°C and a mixture of the oxides was formed. The thermal analysis of that mixture showed that both oxalates were decomposed without any interaction (Fig. 6). Four DTA signals at the temperatures mentioned above were registered, two endothermic signals corresponding to dehydration and two exothermic signals for the oxalate decomposition.

The reaction products after 6 h at 350°C for all compositions are listed in Table 2. In the range $0.5 < x < 2$ defect spinels were formed which can be described by

$$Ni_xMn_{3-x}\square_{3\delta/4}O_{4+\delta} = (4+\delta)/4Ni_{4/(4+\delta)}Mn_{4(3-x)/(4+\delta)}\square_{3\delta/(4+\delta)}O_{4.00} \tag{1}$$

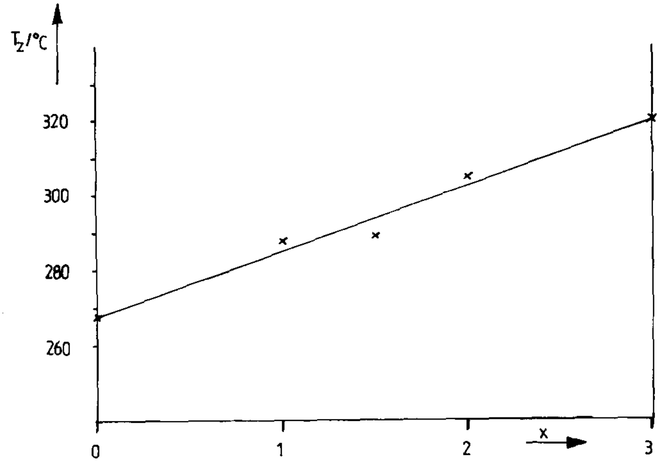


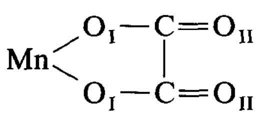
Fig. 7. Dependence of the decomposition temperature on composition.

The decomposition of the oxalate mixed crystals can be described by

$$Ni_xMn_{3-x}(C_2O_4)_3 \cdot 6H_2O + (1+\delta)/2O_2 \rightarrow$$

$$Ni_xMn_{3-x}\square_{3\delta/4}O_{4+\delta} + 3CO + 3CO_2 + 6H_2O \qquad (2)$$

A comparison of the decomposition temperatures of the oxalates in air shows that there is a higher thermal stability with increasing content of nickel (Fig. 7). The temperature at the maximum of the DTG signal was taken as the decomposition temperature. The observed increase of that temperature with the nickel content x follows the increasing electronegativity of the cation. This leads to a higher strength of the $M-O_I$ bond in the oxalate and to a higher thermal stability.



The thermal decomposition of $NiMn_2(C_2O_4)_3 \cdot 6.5H_2O$ in argon also proceeds in two steps. The dehydration finishes at 210°C and the decomposition of the oxalate ends at 400°C. That process is accompanied by an endothermic DTA signal. A mixture of Ni and MnO was found to be the reaction product. The expected mass loss of 63.5% was almost reached. This is in agreement with the results of Tang et al. [3]. The formation of MnO as a result of thermal decomposition of manganese oxalate in a vacuum has been reported [13], together with an endothermic DTA signal at 400°C. The thermal decomposition of nickel oxalate in N_2 has also been investigated; here, Ni was identified as the reaction product [7].

SUMMARY

Mixed crystals of the system $Ni_xMn_{3-x}(C_2O_4)_3 \cdot 6H_2O$ were prepared over the whole composition range $0 < x < 3$. The thermal decomposition of these substances proceeds in two steps. The decomposition of manganese oxalate in air leads to a substance with an approximate composition $MnO_{1.54}$. In the range $0.5 < x < 2$ defect spinels $Ni_xMn_{3-x}\square_{3\delta/4}O_{4+\delta}$ are formed. The thermal stability of the oxalates increases with the nickel content x.

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