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THERMOANALYTIC CHARACTERIZATION OF $NiMn_2O_4$ FORMATION

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Comparative thermogravimetric and heat-flux DSC investigations of phase formations by heating of sinteractive powders, which were prepared by thermal decomposition of a $NiCO_3$: $MnCO_3$ = 1 : 2 mixture and thermal decomposition of oxalate mixed crystals $NiMn_2(C_2O_4)_3.6H_2O$, show the metastability of the defect spinel from the oxalate precursor and its high reactivity.

Dilatometric shrinkage measurements show that reaction sintering leads to the shrinkage and maximum shrinkage rate at lower temperatures. Decomposition of the spinel $NiMn_2O_4$ under NiO separation and O_2 release at 975° in oxygen atmosphere is in contrast to the known phase diagram. Utilization of the thermodynamic driving force of the primarily formed metastable oxide phase and the $NiMn_2O_4$ formation leads, supported by a sinteradditive, to high density semiconductor ceramics.

Ni-Mn-spinels are important in semiconductor ceramic materials. The phase relations were investigated in 1964 by Wickham [1]. Recently the formation of defect spinels after thermal decomposition of oxalate mixed crystals was described [2].

Subject of this paper is the investigation of spinel formation in powders in connection with the sinter densification. As oxygen from the sintering atmosphere participates, thermogravimetry and differential thermal analysis are useful to observe the phase formation processes.

It is of interest to compare the $NiMn_2O_4$-formation from the oxide components NiO, Mn_2O_3 which are prepared by thermal decomposition of $NiCO_3$-$MnCO_3$ mixtures at 600° with the defect spinel, containing the cations at the beginning in homogeneous distribution and prepared by thermal decomposition of oxalate precursors.

It was shown [3], that the preparation of $NiMn_2O_4$ together with the sintering to a dense ceramic microstructure is markedly influenced by the

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impurity content and by additives. Therefore, thermoanalytic characterization was also done for powders containing useful amounts of a sintering aid and shaped by pressing to tablets.

Materials and methods

Starting materials were of reagent grade. Mixtures of $NiCO_3$: $MnCO_3$ in the molar ratio 1:2 had been thermally decomposed at 600° in 6 h. (powder *A*). In the temperature range from 350° up to 450°, during 6 h in flowing air the thermal decomposition of oxalate mixed crystals $NiMn_2(C_2O_4)_3.6H_2O$ was performed [2] (powder *B*).

The sintering promotion was investigated with 1 w-% $Pb_5Ge_3O_{11}$ wet milled with the powder.

Powder mixtures without sintering aid are denoted with the index O (A_O, B_O), those with sintering aid with the index 1 (A_1, B_1). Decomposition products were characterized by means of specific surface determination with nitrogen BET-method. Sedimentation (Sedigraph 5000 D, Micromeritics) of the powders, dispersed in water with NaK-hexametasphoshate and ultrasonics shows strong agglomeration.

Pressing of the powders, also for thermoanalytic characterization of tablets 5 mm in diameter and about 2 mm thick, was done according to the following laboratory techniques:

- powder wet mixing with 0.25 w-% PVA
- pressing the moist powder through a mesh
- shaping of tablets of 10 mm in diameter with 80 MPa
- crushing
- sieving separation of the fraction 80-630 μm
- final pressing in a 5 mm steel die with 150 MPa.

Granules bulk densities and the densities of pressed tablets were controlled volumetrically.

Thermal analysis was performed with 10 deg/min heating and cooling rate under air or oxygen using simultaneous TG, heat-flux DSC (NETZSCH STA 429) and additionally dilatometry (NETZSCH DIL 402). Starting from the investigation of powders, the phase formation processes in pressed tablets were observed in-situ during the heating up and sintering of the samples. Quenched 10 mm tablets from the TA-furnace were investigated by X-ray diffraction (Carl Zeiss Jena HZG4, CuK_α radiation).

Formation of the spinel $NiMn_2O_4$

The investigations are illustrated at 3 levels. Starting from the investigations of powders *A* and *B* with TG and XRD, influence of pressing compaction and the correlation between shrinkage - phase formation will be demonstrated.

Phase formation

After decomposition of $NiCO_3 : MnCO_3 = 1 : 2$ at 600° NiO, Mn_2O_3 and some $NiMnO_3$ are obtained. The specific surface area of this powder mixture is 12 m^2/g. Figure 1a together with Fig. 2 show, that further $NiMnO_3$ is formed during heating up with 10 deg/min in O_2 from 700° to 780°.

$$2\,NiO + Mn_2O_3 + 1/2\,O_2 \rightarrow 2\,NiMnO_3 \qquad (1)$$

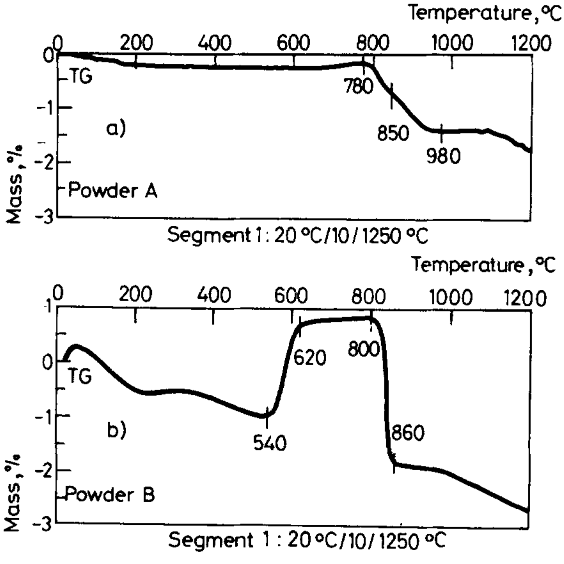

Fig. 1 TG of tablets (diameter 10 mm, weight 250 mg) in oxygen with 10 deg/min heating rate; a) - powder A_0, b) - powder B_0 temperatures indicate sample quenching for XRD, see Figs 2 and 3

$NiMnO_3$ with an Ilmenite type structure cannot be identified in samples, which were heated to temperatures higher than 850°, because it reacts with Mn_2O_3 to $NiMn_2O_4$ under oxygen loss.

$$2\,NiMnO_3 + Mn_2O_3 \rightarrow 2\,NiMn_2O_4 + 1/2\,O_2 \qquad (2)$$

The formation of $NiMn_2O_4$ can be mentioned by weight loss in Fig. 1a. As heat-flux DSC shows (Fig. 7), the solid state reaction to the spinel $NiMn_2O_4$ is a 2-step reaction. Under the dynamic regime with 10 deg/min heating rate to 980°' almost only $NiMn_2O_4$ can be identified. We suppose, that at first $NiMnO_3$ reacts (Eq. 2) and then NiO is incorporated into the reaction with Mn_2O_3.

$$NiO + Mn_2O_3 \rightarrow NiMn_2O_4 \qquad (3)$$

In dependence from temperature and time of decomposition of the oxalate mixed crystals, metastable $NiMn_2O_4$-powders of various specific surfaces and compositions can be prepared. After 6 h decomposition at 350° in flowing air, a cubic defect spinel phase of the composition $Ni_{0.96}Mn_{1.91}\square_{0,13}O_4$ with high reactivity is obtained. The specific area is 50 m^2/g.

Figure 1b shows weight loss by removing adsorbed humidity and defect diminishing by oxygen release. The decomposition of the metastable spinel to form $NiMnO_3$ and Mn_2O_3 occurs between 540° and 620° under oxidation.

$$NiMn_2\square\frac{3\delta}{4}O_{4+\delta} + \frac{1-2\delta}{4}O_2 \rightarrow NiMnO_3 + 1/2\,Mn_2O_3 \qquad (4)$$

Between 800° and 860° this very intimate mixture reacts to form the spinel $NiMn_2O_4$ (Eq. 2). With a heating rate of 10 deg/min the spinel decomposition (Eq. 4) seems to be nearly complete. The mass change shown in Fig. 1b indicates that the reaction comes to an end. This indicates high reactivity.

By comparing Fig. 1a with Fig. 1b can be concluded that the $NiMn_2O_4$ formation starting from the oxalate precursor is completed at lower temperature (860°) than from the powder mixture *A* (980°), where the reaction remained incomplete. XRD patterns shown in Figs 2 and 3 verify that fact.

Remarkable in Fig. 1b is the further weight loss beginning at 975°, probably indicating the spinel decomposition under oxygen release and NiO

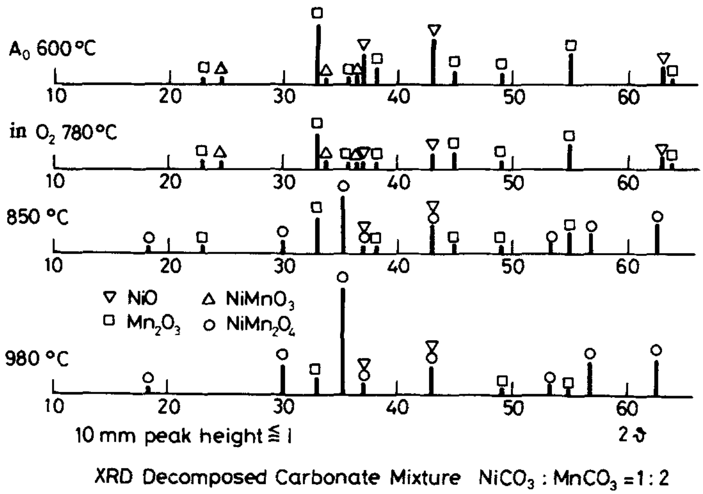

Fig. 2 XRD-pattern of tablets A_0, sample quenching is indicated in Fig. 1a

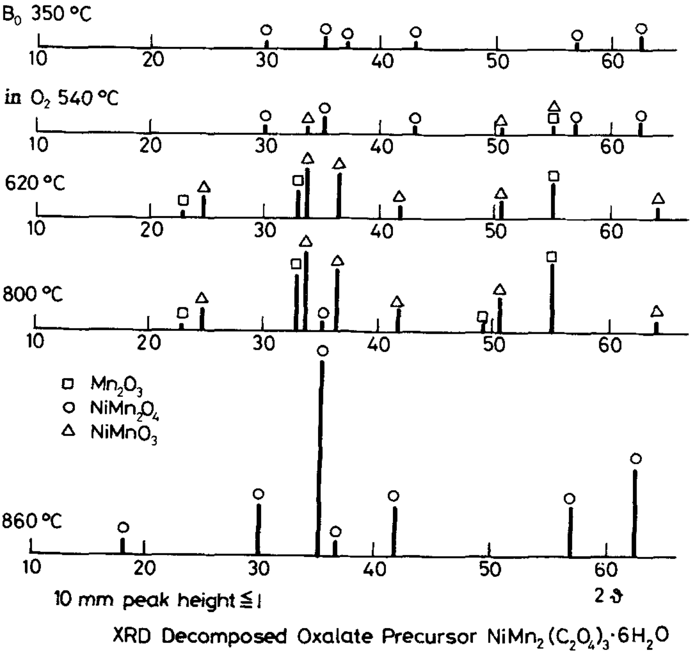

Fig. 3 XRD-pattern of tablets B_0, sample quenching is indicated in Fig. 1b

separation.

$$NiMn_2O_4 \rightarrow x\ NiO + \frac{3-x}{3} Ni^{II}_{(3-3x)/(3-x)} Mn^{II}_{2x/(3-x)} Mn^{III}_2 O_4 + x/6\ O_2 \tag{5}$$

Hence the temperature of decomposition of $NiMn_2O_4$ in oxygen (1100°) in the phase diagram by Wickham has to be improved [4]. As in the case of powder *A* changes in oxygen partial pressure influences the reactions according to law of mass action. That means, the oxidation occurs at higher temperatures in air, the reduction, however, at lower temperatures in comparison with O_2.

Influence of compaction

Starting powder, press granules, and tablets were measured under the same conditions with TG-heat-flux DSC to find out the influence of powder compaction density on the phase formation. Figures 4 and 5 show that for powder B_0 no difference in the thermal behaviour between powder, granules, tablet can be observed during heating up with 10 deg/min in O_2. The porosity is high enough for free oxygen gain and loss. In Fig. 5 can be seen that the calculated weight loss (Eq. 2) is the completer, the higher the densification. The oxygen loss in the spinel formation increases with densification up to the value of 3.3 w-% corresponding to Eq. 2. Confirmed by XRD-diffraction patterns (Fig. 3) it can be concluded that the close contact of $NiMnO_3$ and Mn_2O_3 favours the complete reaction of the spinel under the heating rate of 10 deg/min up to 860°.

Decomposition of the spinel with NiO separation and O_2 release (Fig. 5) starts independently of the density at 975°. Figure 6 and 4 show the difference between powder A_1 with the sintering aid and the powder B_0 with uniform phase composition and high reativity. Two overlapping endothermal reaction steps are obvious, Fig. 6 the first can be described by Eq. 2 and the second probably by Eq. 3.

For powder A_1 it was found that under the effect of the sintering aid the packing density of the powder mixture does not change starting and end temperatures of the reactions, but influences the relative rates of the two reactions compared to each other. The partial reaction according to Eq. 2 can be recognized at lower temperatures by means of an endothermal en-

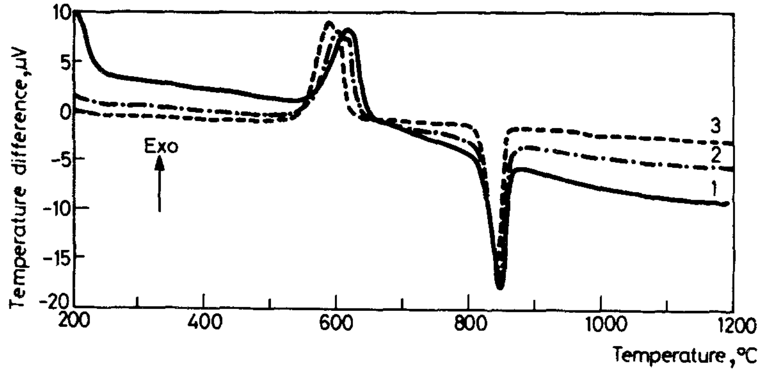

Fig. 4 Heat-flux DSC of B_0 as powder, granule, tablet in oxygen with 10 deg/min heating rate, various sample weights (24 up to 91 mg) scaled to 24 mg

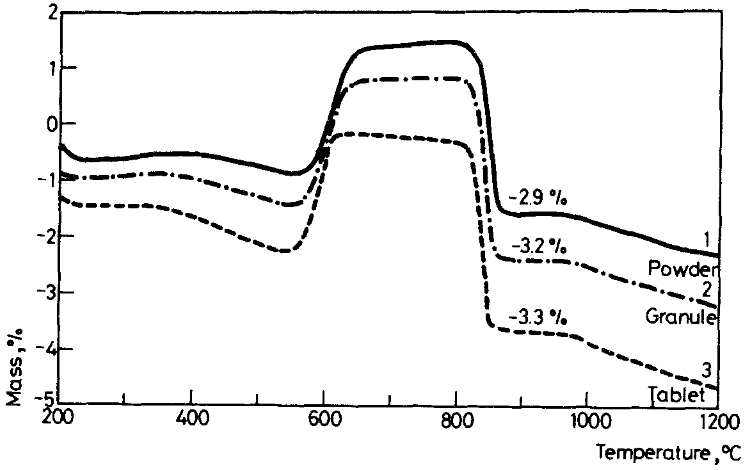

Fig. 5 TG simultaneous measured with heat-flux DSC (Fig. 4)

thalpy effect if the sample density is higher. Nearly complete conversion under formation of uniform $NiMn_2O_4$ phase is reached at 980°.

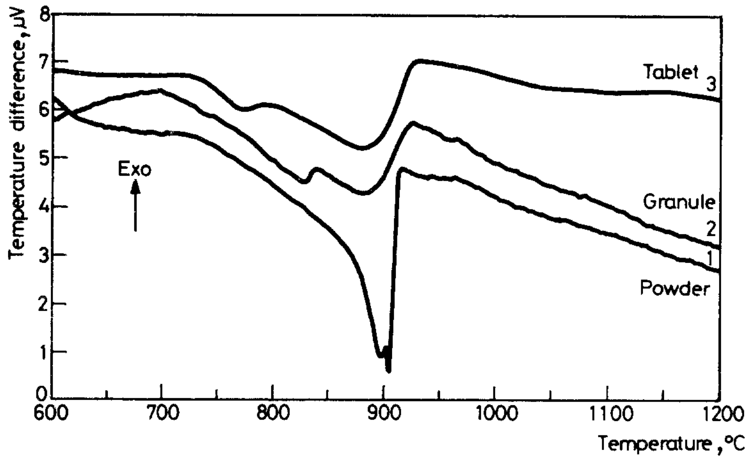

Fig. 6 Heat-flux DSC of A_1 as powder, granule, tablet in air with 10 deg/min heating rate, various sample weights (24 to 102 mg) scaled to 24 mg

Shrinkage as a result of solid state reactions to form $NiMn_2O_4$

The described method of powder pressing leads for powder *A* (12 m^2/g) and *B* (10-18 m^2/g) to reproducible green densities, of about 50% of the theoretical density (5.29 g/cm^3).

This starting situation made possible comparable shrinkage investigations of both powders, without correction concerning various initial densities.

The powder *B* with 50 m^2/g after 350° decomposition of the oxalate mixed crystals was densified under the described conditions only to 38-40% of the theoretical density. In spite of such bad starting situation for the sintering densification this powder was included into the dilatometric investigations.

Provided a homogeneous powder packing without grain orientation in the powder compact and equal X-ray densities of the powder and sintered ceramics, there is the following relationship between packing density and possible shrinkage:

$$\Delta l / l_0 = 1 - C^{0.33} \text{ (C-packing density} < 1)$$

So 20.4% shrinkage can be expected of 50% packing density, respectively 26.1% shrinkage of 40% packing density. Usual axial pressing leads to a

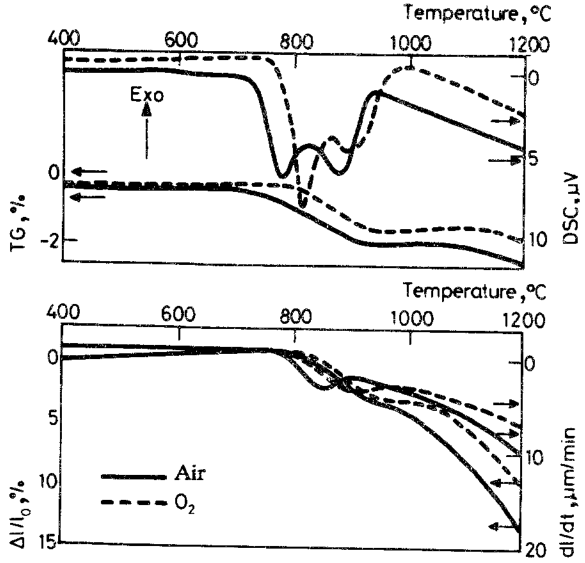

Fig. 7 A_0 tablets (5 mm diameter, 100 mg weight) in air and oxygen, 10 deg/min, upper part - TG, heat-flux DSC; lower part - shrinkage, shrinkage speed

grain orientation and thus to higher shrinkage in height than in diameter. The possible increase in shrinkage measured in the dilatometer as a result of probe piston force explains the shrinkage values which are a little higher than 20%. Possible changes of materials densities during the phase formation of $NiMn_2O_4$ are not taken into account in the following comparison of the densification behaviours of the powders *A* and *B*.

Figure 7 shows, in the lower part, the curves for shrinkage and shrinkage speeds of powder compacts A_0 in air and oxygen, and in the upper part the corresponding mass changes and thermal effects. According to the law of mass action, the beginning of the reaction with oxygen loss occurs at lower temperatures in air. It is easy to observe that shrinkage of pressed powder tablets starts by 30 K higher the indicated by weight loss and endothermic doublepeak start of the $NiMn_2O_4$ formation.

The ratio of shrinkage per time shows a slight maximum. It is at 900° for sintering in O_2, at 850° in air. When the spinel formation is complete, shrinkage will accelerate again. Therefore the phase formation of $NiMn_2O_4$ effects the shrinkage of the ceramic bodies.

For tablets A_0 the weight loss resulting from spinel decomposition (Eq. 5) is only slight above 1100° in oxygen and 1050° in air. Figure 8 shows the results for tablets A_1. Under the influence of the sintering aid, solid state reactions between NiO, Mn_2O_3, $NiMnO_3$ starts in the tablets approximately by 20 K lower than in the case of A_0. Shrinkage starts at lower temperature as well. The influence of the sintering atmosphere retains.

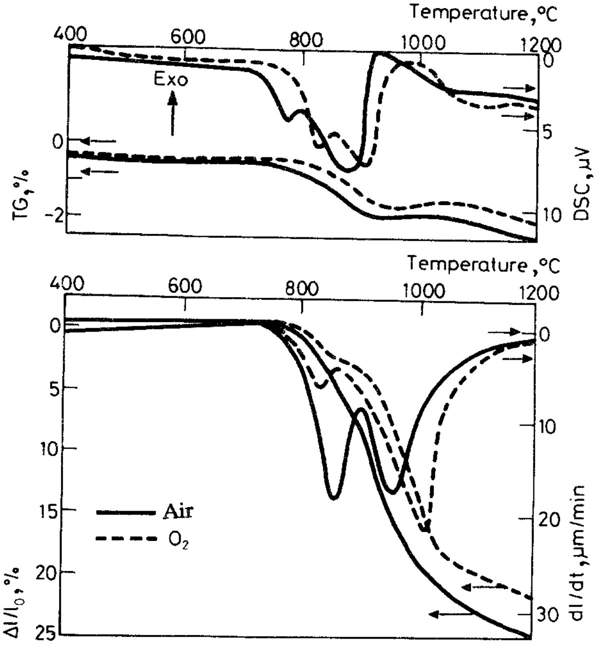

Fig. 8 A_1 tablets (5 mm diameter, 100 mg weight) in air and oxygen, 10 deg/min, upper part - TG, heat-flux DSC; lower part - shrinkage, shrinkage speed

The first shrinkage maximum related with $NiMn_2O_4$ formation is distinctly under the influence of the sintering aid. Additionally, a second maximum of the shrinkage speed is caused at 950° in air and at 1000° in O_2. So it can be attained, that at the end of the temperature rise the possible total shrinkage is reached up to 90%. Fast-sintering conditions with 50 deg/min heating rate do not lead to more shrinkage. Although the solid state reaction forming the spinel $NiMn_2O_4$ is endothermic (for thermodynamic values see [5]), it is so fast even at low heating rates that rate controlled sintering with 0.1 μm/s shrinkage rate was not possible.

Elevated sinteractivity of the defect spinel during heating up in the powders B_0 (Fig. 9) and B_1 (Fig. 10) can be seen in comparison with Figs 7, 8.

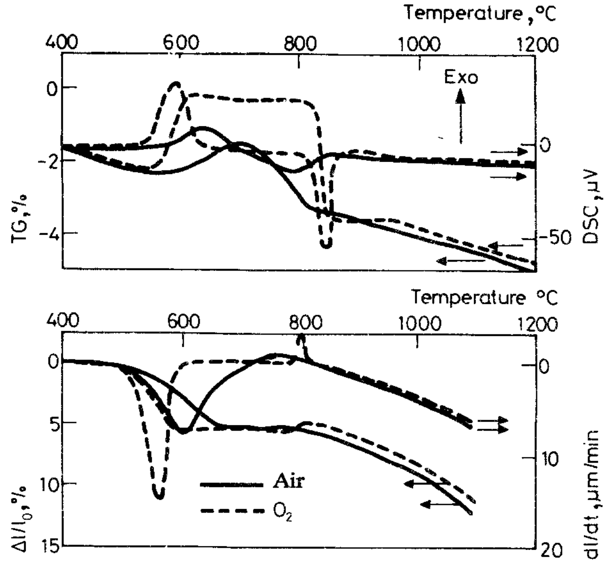

Fig. 9 B_O (50 m^2/g) tablets (5 mm diameter, 100 mg weight) in air and oxygen, 10 deg/min heating rate; upper part - TG, heat-flux DSC; lower part - shrinkage, shrinkage speed

The upper part of Fig. 9 for B_O with 50 m^2/g specific surface indicates that the decomposition of the defect spinel phase under air and 10 deg/min remains incomplete. Corresponding shrinkage investigations in the lower part of Fig. 9 show that decomposition of the defect spinel leads to shrinkage of the powder compact. Even if the solid state reaction of renewed spinel formation (Eq. 2) is not related to diminishing of the molar volume, calculated by using X-ray densities, a sligthly intermediate swelling of tablets is measured with the help of dilatometry. Afterwards the sintering of the well crystallized spinel at 860° comes into effect. Because of the low green density (38-40%) the sintering behaviour with very high total shrinkage is unfavourable.

From Fig. 10 in comparison with Fig. 9 it becomes obvious, that powder B_1 with a lower specific surface (10 m^2/g) at 10 deg/min does not clearly undergo decomposition and new formation of the spinel phase. Enthalpy effects and mass changes are kinetically inhibited and occur less (cf. the other scale of thermocurrent).

The concentration of cation defects in the defect spinel powder heated up to 450° is much lower (nearly 1/4). The decomposition of the defect spinel phase to form $NiMnO_3$ and Mn_2O_3 (Eq. 4) and the formation of

$NiMn_2O_4$ (Eq. 2) above 700° are not clearly distinct under 10 deg/min heating rate in oxygen. This indicates a markedly lowered reactivity in this containing sintering aid sample.

The comparison of Figs 9 and 10 in the lower part shows that the shrinkage of the tablets from powder B_1 (10 m^2/g) is suppressed between 500° and 700°, whereas the shrinkage is more effective in the temperature range of thermal stability of $NiMn_2O_4$ (700°-975°).

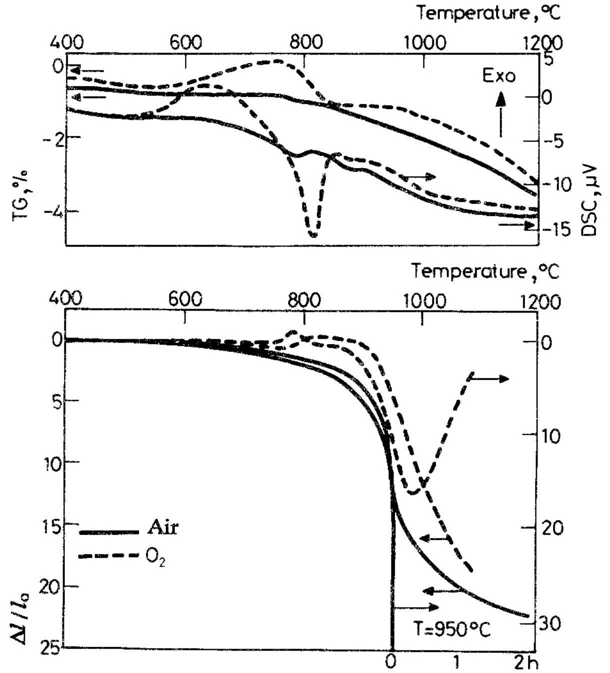

Fig. 10 B_1 (10 m^2/g) tablets (5 mm diameter, 100 mg weight) in air and oxygen, 10 deg/min heating rate; upper part - TG, heat-flux DSC; lower part - shrinkage, shrinkage speed. For B_1 sintering in air (fat line) from 950°C is plotted isothermal sintering at this temperature

Higher green density (50%) of this powder supports this result. Decomposition of a defect spinel with lower defect state takes place in oxygen atmosphere under dynamic conditions only partially. In air there is no decomposition under oxygen gain indicated by thermogravimetry.

Because the maximum of shrinkage speed is at 950°, isothermal sintering at 950-1000°, leads to high density spinel ceramics, if the raw materials are converted by preparation *B*, precipitation of oxalate mixed crystals and their thermal decomposition.

Conclusion

First experiments had shown slow sintering of $NiMn_2O_4$ powders prepared by calcination at high temperatures. Powders *A* and *B* from decomposed carbonates and oxalate mixed crystals with large specific surface, undergoing phase formation processes during heating up, are sinteractive powders without any grinding or milling.

Dilatometric shrinkage investigation parallel to TG, DTA, XRD analysis of phase formation describes the sintering behaviour of powders *A* and as reaction sintering. It could be shown that the dry pressed tablets shrink during heating up as a result of solid state reactions from various starting situations to the spinel $NiMn_2O_4$.

The spinel $NiMn_2O_4$ from the powder mixture *A* is formed nearly completely at 980° after heating up with 10 deg/min in oxygen. In contrast to the powder mixture *A*, for the metastable defect spinel powder *B* the complete formation of the spinel is proved even at 860°.

The mixture of NiO, Mn_2O_3, $NiMnO_3$ (powder *A*) activated by the sintering aid sinters in two steps, inclusive the value of reaction sintering at the beginning of the densification at 730°. As a result of the decomposition of the metastable spinel (powder *B*) it starts to shrink by 150 K lower than powder mixture *A*. The maximum of shrinkage rate is observed at 950°, that means 50 K lower than that of powder *A*.

Decomposition of $NiMn_2O_4$ in oxygen starts already at 975° and not at 1100° as indicated in the phase diagram [1]. The subject of a further publication [4] will be the influence of the spinel decomposition under NiO-separation and oxygen release on the densification and microstructural development by inducing lattice mobility.

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Zusammenfassung – Vergleichende thermogravimetrische und Wärmefluß-DSC Untersuchungen der Phasenbildungsprozesse beim Aufheizen sinteraktiver Pulver, erhalten aus der thermischen Zersetzung von $NiCO_3$:$MnCO_3$ = 1:2 Mischungen bzw. Zersetzung von Oxalatmischkristallen $NiMn_2(C_2O_4)_3.6H_2O$ zeigen die Metastabilität des Defektspinells aus der Oxalatvorstufe, sowie seine erhöhte Reaktivität. Wie dilatometrische Schwindungsmessungen belegen, führt das reaktive Sintern zum Schwindungsbeginn und Maximum der Schwindungsgeschwindigkeit bei erniedrigter Temperatur. Die Zersetzung des Spinells $NiMn_2O_4$ unter NiO Ausscheidung und Sauerstoffabgabe ab 975°C in Sauerstoffatmosphäre steht im Widerspruch zum bekannten Phasendiagramm. Bei Nutzung thermodynamischer Triebkräfte primär entstandener metastabiler Oxidphase und der $NiMn_2O_4$ Bildung werden, unterstützt durch den Zusatz von Sinterhilfsmittel, Halbleiterkeramiken hoher Dichte erhalten.