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Synthesis of magnesium stannates by thermal decomposition of peroxo-precursors

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Abstract

Magnesium orthostannate Mg_2SnO_4 can be synthesized at 900°C with high purity using the peroxide route. The powder shows large specific surface area and small grain size, leading to high sinterability. A peroxo-precursor is formed during the synthesis by a precipitation step from aqueous solution. The thermal decomposition of the X-ray amorphous precursor leads directly to Mg_2SnO_4. Magnesium metastannate $MgSnO_3$ is formed after thermal degradation of a corresponding peroxo-precursor at temperatures below 700°C. Further thermal treatment at temperatures above 700°C leads to the decomposition of $MgSnO_3$ to Mg_2SnO_4 and SnO_2.

INTRODUCTION

The phase equilibria in the $MgO-SnO_2$ system have been studied by several authors, and the existence of the stable phase Mg_2SnO_4 has been been described [1-4]. It has been shown that the composition $MgSnO_3$ can be obtained only at lower temperatures [3, 5-9]. This metastable phase decomposes to Mg_2SnO_4 and SnO_2 at temperatures above 800°C. Magnesium orthostannate, with its nearly perfect inverse spinel structure, is normally synthesized by solid-state reaction between MgO and SnO_2 at temperatures of about 1100-1200°C [1-8]. The equilibrium phase of Mg_2SnO_4 was therefore prepared by sintering of oxide mixture pellets at 1200°C in a platinum boat under air for 24 h [5]. Obtaining phase-pure magnesium metastannate seems to be difficult because of the low decomposition temperature [3, 5-9]. The dehydration of $Mg[Sn(OH)_6]$ at 300°C is the only method described for the preparation of pure $MgSnO_3$ [10]. There are no publications up to now describing experiments for the synthesis of Mg_2SnO_4 by wet chemical methods. On the other hand, barium stannates or magnesium titanates of various compositions can be synthesized using the peroxide route [11, 12].

This paper details the synthesis of Mg_2SnO_4 and $MgSnO_3$ via the peroxide process. The precipitation of the magnesium- and tin-containing precursors, their thermal decomposition to the magnesium stannates and the characterization of both intermediate products and the final stannate powders are described here, as well as the results from sintering experiments.

EXPERIMENTAL

Preparation of samples

An aqueous solution of $MgCl_2 \cdot 6H_2O$ (E. Merck, Darmstadt) and $SnCl_4$ (E. Merck, Darmstadt; Sn concentration 0.6 mol/l) was added rapidly at 10°C under argon to a larger volume ($\times 1.5$) of a solution of H_2O_2 and ammonia in water. The molar ratios of $MgCl_2 \cdot 6H_2O : TiCl_4 : H_2O_2 : NH_3$ used were 1:1:2.5:12 for $MgSnO_3$ and 2:1:5:12 for Mg_2SnO_4. Light yellow amorphous precipitates were formed. The precipitates were filtered off, washed with water and then dried over H_2SO_4 in a desiccator. The resulting precursors were calcined in air at temperatures up to 900°C. In addition, Mg_2SnO_4 was prepared using the solid-state reaction at 1200°C starting from reagent grade MgO and SnO_2 (E. Merck, Darmstadt) [5].

The chemical analysis of the dried precipitates and of the powders obtained after calcination for 1 h at 900°C was performed as follows. Tin was determined gravimetrically as SnO_2, and magnesium was titrated complexometrically with ethylenediaminetetraacetic acid (EDTA). The peroxide content was analysed iodometrically.

Apparatus

Thermogravimetric analysis (TG)

A Thermogravimetric Analyzer 951 system (Du Pont Instruments) was used with a heating rate of 600°C/h.

Differential thermal analysis (DTA)

The Thermal Analyst System 2100 (Du Pont Instruments) was used with a heating rate of 300°C/h.

X-ray powder diffraction (XRD)

A Philips PW 1710 diffractometer was used with a Ni filter and Cu Kα radiation.

Determination of impurities

Certain impurities were measured using atomic absorption spectrometry (AAS) with a Perkin Elmer 303 instrument and atomic emission spectrometry (AES) with a PGS 2 apparatus (Carl Zeiss Jena).

B.E.T. measurements

Surface characterization was carried out by B.E.T. measurements using nitrogen adsorption (Accusorb 2100 D, Micromeritics).

Sintering studies

The two different Mg_2SnO_4 powders were investigated with respect to their sintering behaviour. The powders were mixed with a binder solution (65% H_2O, 25% glycerol, 10% polyvinyl alcohol (PVA)) in a mortar, deagglomerated for 20 min in a ball mill, dried and passed through an 80 mesh sieve. After sieving, the powders were compressed into discs under a pressure of 125 MPa and sintered at 1200 and 1400°C. The densities of the specimens were determined by weighing and measuring their dimensions using a micrometer before and after each heating step.

RESULTS AND DISCUSSION

Table 1 contains the results of the analysis of the dried precursors and of the powders obtained after calcination at 900°C. The peroxo-precursors show stoichiometric composition and so do the stannates. The reactions of precursor formation can be summarized by the following equations:

$$MgCl_2 + SnCl_4 + H_2O_2 + 6NH_3 + 5H_2O \rightarrow MgSnO_2(O_2) \cdot 3H_2O + 6NH_4Cl \tag{1}$$

$$2MgCl_2 + SnCl_4 + H_2O_2 + 8NH_3 + 8H_2O \rightarrow Mg_2SnO_3(O_2) \cdot 5H_2O + 8NH_4Cl \tag{2}$$

TABLE 1

Analytical data for the peroxo-precursors and for the products obtained after thermal decomposition at 900°C (weight loss for 1 h at 900°C)

Component	(% exp.)	(% calc.)	(% exp.)	(% calc.)
	$MgSnO_2(O_2) \cdot 3H_2O$		"$MgSnO_3$"	
Magnesium	9.2	9.3	12.6	12.7
Tin	45.6	45.5	62.2	62.1
Peroxide	12.0	12.3	–	–
Weight loss	27.0	26.8	–	–
	$Mg_2SnO_3(O_2) \cdot 5H_2O$		Mg_2SnO_4	
Magnesium	14.3	14.4	20.9	21.0
Tin	35.1	35.2	51.3	51.3
Peroxide	9.3	9.5	–	–
Weight loss	31.8	31.4	–	–

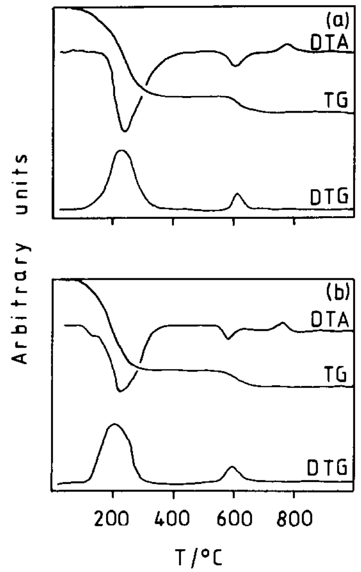

Fig. 1. DTA, TG and DTG curves for (a) $MgSnO_2(O_2) \cdot 3H_2O$ and (b) $Mg_2SnO_3(O_2) \cdot 5H_2O$.

The TG, DTG and DTA curves of the thermal degradation of the two precursors are shown in Fig. 1. Two stages of weight loss can be observed in both cases. In a first step up to 350°C, the water is evaporated (endothermic effect). The decomposition of the peroxide groups occurs between 500 and 650°C and oxygen is released (endothermic effect). An exotherm above 700°C observed in each case is attributed to the crystallization of stannate and oxide phases. The continuation of the thermal treatment at higher temperatures is accompanied by a decrease of the specific surface area of the powders. Table 2 shows the results of B.E.T. measurements including the calculated mean particle sizes for the powders formed during the thermal degradation of the peroxo-precursor $Mg_2SnO_3(O_2) \cdot 5H_2O$.

X-ray diffractograms for the decomposition products of the two peroxo-precursors are shown in Fig. 2 for different calcination temperatures (in

TABLE 2

Specific surface area and mean particle diameter dependence on the calcination conditions for the powders obtained during Mg_2SnO_4 formation

Conditions (h/°C)	Specific surface area in m^2/g	Mean particle diameter in μm
8/200	115	0.01
8/400	91	0.01
8/600	56	0.02
8/800	36	0.03
8/900	22	0.06

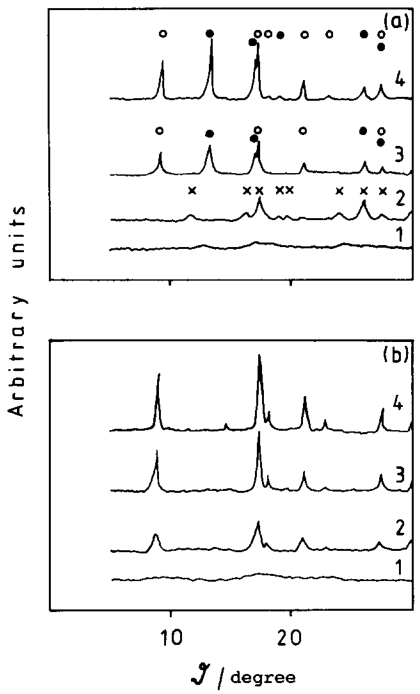

Fig. 2. X-ray diffractograms of the decomposition products of (a) $MgSnO_2(O_2) \cdot 3H_2O$ and (b) $Mg_2SnO_3(O_2) \cdot 5H_2O$; (×) $MgSnO_3$, (○) Mg_2SnO_4, (●) SnO_2.

each case with calcination for 8 h). The two precursors and the powders obtained after heating to 500°C are X-ray amorphous. A similar situation has been observed for the peroxo-precursors for barium stannates [11] as well as for various alkaline earth metal titanates [12–19]. Small broad reflections appear at 550°C, indicating the formation of stannate phases. The precursor $Mg_2SnO_3(O_2) \cdot 5H_2O$ is directly decomposed to Mg_2SnO_4. At temperatures above 500°C, the reflections of only this stannate phase can be indicated. Mg_2SnO_4 is obtained in its pure form upon calcination at 900°C for 1 h. No further formation of other phases can be observed at temperatures above 900°C. Analogous behaviour has been indicated previously for the formation of $BaSnO_3$ and of magnesium, calcium and strontium titanates starting from peroxo-precursors [11, 12, 17, 18].

Another situation has been found for the thermal degradation of the precursor $MgSnO_2(O_2) \cdot 3H_2O$. Heating above 550°C leads to the formation of $MgSnO_3$. At 700°C, all strong reflections of the metastannate can be observed in the diffractogram. Only very small reflections of SnO_2 and Mg_2SnO_4 can be indicated in addition to $MgSnO_3$. The amounts of SnO_2 and Mg_2SnO_4 increase at temperatures above 700°C. The diffractogram for the powder obtained after thermal treatment at 900°C shows only the presence of the phases SnO_2 and Mg_2SnO_4. No $MgSnO_3$ reflections can be observed for samples calcined at 900°C and above. The formation of magnesium metastannate from the amorphous phase at such relatively low temperatures and its decomposition above 700°C is remarkable and confirms the former findings as to the metastability of this composition [3, 5-9]. The formation of pure $MgSnO_3$ is very difficult, suggesting that the persistence of the orthostannate into the field of stability of the metastannate is an indication of inequilibrium and possibly of metastability.

The results of sintering experiments are shown in Fig. 3. Magnesium orthostannate synthesized using the peroxide route on the one hand (Mg_2SnO_4 PR) and the mixed oxide route on the other (Mg_2SnO_4 MOR) were sintered in air at 1200 and 1400°C. Table 3 shows some results of surface investigations and analytical measurements for the two Mg_2SnO_4 powders used for the sintering experiments. The different starting densities ρ_0 of the compacted powders (2.25 g/cm^3 for Mg_2SnO_4 PR and 2.62 g/cm^3 for Mg_2SnO_4 MOR) are included by using the densification parameter $\alpha = (\rho_t - \rho_0)/(\rho_{th} - \rho_0)$ (ρ_t = density at a given time, ρ_{th} = theoretical density). Isothermal sintering at 1200 and 1400°C leads to good densification, especially in the case of the peroxide-derived product. The densities after 4 h

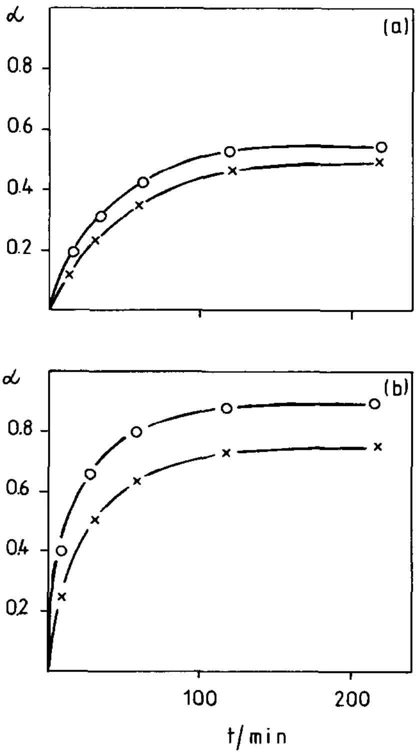

Fig. 3. Densification parameter of (○) Mg_2SnO_4 PR and (×) Mg_2SnO_4 MOR compacts as a function of isothermal heating time at (a) 1200°C and (b) 1400°C.

TABLE 3

Surface area and analytical data of two Mg_2SnO_4 powders used for the sintering experiments

	Specific surface area in (m^2/g)	d_{BET} in μm	Impurity in ppm				
			Al	Si	Fe	Ca	Sr
Mg_2SnO_4 PR	29	0.04	80	40	–	40	20
Mg_2SnO_4 MOR	5	0.25	160	90	90	60	50

at 1200°C are 3.64 g/cm^3 (76% of ρ_{th}) for Mg_2SnO_4 PR and 3.70 g/cm^3 (78%) for Mg_2SnO_4 MOR. The shrinkage of the compacts is more marked at 1400°C, leading to density values of 4.52 g/cm^3 for Mg_2SnO_4 PR (95%) and 4.25 g/cm^3 for Mg_2SnO_4 MOR (89%).

The results show that the peroxide process here described can be used for the preparation of very sinter-active Mg_2SnO_4 and electroceramic elements at distinctly lower temperatures than those necessary for the conventional solid-state reaction.

CONCLUSIONS

This work shows that it is possible to synthesize magnesium orthostannate Mg_2SnO_4 by the peroxide route at low temperatures. The first step of the preparation is the precipitation of a peroxo-precursor, which is transformable into the stannate by thermal decomposition. Large specific surface area and a very small grain size of the stannate powder lead to a high sinterability, which is significantly better than in the case of Mg_2SnO_4 synthesized by the solid-state reaction. $MgSnO_3$ can be obtained after thermal degradation of a corresponding peroxo-precursor as a metastable phase at temperatures below 700°C.

REFERENCES

1 G. Natta and L Passerini, Atti Accad. Naz. Lincei, Cl. Sci., Fis. Mat. Nat., Rend., 9 (1929) 557.
2 W.W. Coffen, J. Am. Ceram. Soc., 36 (1953) 207.
3 G.T. Faust and W.T. Schaller, Z. Kristallogr., 134 (1971) 116.
4 I.N.S. Jackson, R.C. Liebermann and A.E. Ringwood, Earth Planet. Sci. Lett., 24 (1974) 203.
5 S. Raghavan, Thermochim. Acta, 122 (1987) 389.
6 L.W. Coughanour, R.S. Roth, S. Marzullo and F.E. Sennett, J. Res. Natl. Bur. Std., 54 (1955) 149.
7 Y. Tanaka, Bull. Chem. Soc. Jpn., 16 (1940) 1023.
8 Y. Tanaka, Bull. Chem. Soc. Jpn., 17 (1942) 64.
9 A.L. Smith, J. Am. Chem. Soc., 82 (1960) 3502.
10 T. Dupuis and V. Lorenzelli, C.R. Acad. Sci., 259 (1964) 4585.

11 G. Pfaff, J. Eur. Ceram. Soc., 12 (1993) 159.
12 G. Pfaff, Ceram. Int., in press.
13 G. Pfaff, Z. Chem., 28 (1988) 76.
14 G. Pfaff, J. Mater. Sci. Lett., 9 (1990) 1145.
15 G. Pfaff, J. Mater. Sci. Lett., 10 (1991) 129.
16 G. Pfaff, J. Mater. Sci. Lett., 10 (1991) 1059.
17 G. Pfaff, J. Eur. Ceram. Soc., 9 (1992) 121.
18 G. Pfaff, J. Eur. Ceram. Soc., 9 (1992) 293.
19 G. Pfaff, J. Mater. Sci. Lett., 12 (1993) 32.