MECHANOCHEMISTRY AND MECHANICAL ALLOYING 2003

JOURNAL OF MATERIALS SCIENCE **39** (2004) 5239 – 5242

The influence of grinding conditions on the mechanochemical synthesis of zinc stannate

N. NIKOLIC*
Institute of Technical Sciences of SASA, Knez-Mihailova 35/IV, 11000 Belgrade, Serbia and Montenegro
E-mail: natali@itn.sanu.ac.yu

Z. MARINKOVIC, T. SRECKOVIC
Center for Multidisciplinary Studies, University of Belgrade, Kneza Viseslava 1a, 11000 Belgrade, Serbia and Montenegro

The aim of this work is the investigation of experimental conditions for mechanochemical synthesis of spinel zinc stannate (Zn_2SnO_4). Application of this material include manufacturing of CO, H_2, NO, NO_2, i-C_4H_{10} and C_2H_5OH gas sensors, production of transparent conducting electrodes, window coatings and anode for use in photoelectrochemistry. Starting powder mixtures of zinc oxide and tin oxide in the molar ratio, in accordance with the stoichiometrics of spinel zinc stannate, were mechanically activated by grinding in a planetary mill for various periods of time in the interval of 0 to 160 min. Changes of physico-chemical characteristics and microstructural parameters in the ZnO-SnO_2 system after grinding were followed using surface area analysis and X-ray powder diffraction, while thermal behavior was examined by differential thermal analysis and sensitive dilatometer. The beginning of zinc stannate phase formation was noticed after 40 min of grinding, and prolonged grinding leads to the formation of spinel zinc stannate as the major phase with insignificant amount of unreacted zinc oxide and tin oxide. The formation of spinel was accelerated with the increase of sintering temperature, and monophased zinc stannate was obtained when powder mixture was grinded for 160 min followed by sintering at 1200°C. *© 2004 Kluwer Academic Publishers*

1. Introduction

Spinel zinc stannate (Zn_2SnO_4) and zinc stannate-based materials exhibit sensor properties (detection of combustible gases and humidity) [1], and can also be used for fabrication of electrical contacts, transparent electrodes and window coatings, and in electrochemistry [2–4].

Spinel type zinc stannate is a ternary oxide ($Zn^{II}[Zn^{II}Sn^{IV}]O_4$), while the perovskite type zinc stannate ($ZnSnO_3$) is unstable and decomposes into Zn_2SnO_4 and SnO_2 at temperatures higher than 700°C [5, 6]. Many processing routes, including spray pyrolysis, rf magnetron sputtering, sol-gel method etc. have been used to synthesize spinel zinc stannate-based thin films [7–9]. Zinc stannate composite-based materials also show interesting sensor characteristics [10]. Zinc stannate powders were synthesized by calcination of a stoichiometric mixture of ZnO and SnO_2 at 1000°C for 48 h, after the mixture was mechanically activated in a ball mill for 12 h [11]. Using hydrothermal method and solution with a Zn:Sn = 7:3 ratio, Fang *et al.* obtained zinc stannate at 220°C after 72 h [12], while nano-sized Zn_2SnO_4 powders were obtained at 244°C using the coprecipitation method [13].

Mechanical activation by grinding is a widely used process in the field of powder processing and alloying [14, 15]. Investigations on chemical reactions between oxides point to the fact that those are especially hard to perform due to their structure and properties, and a new branch of so-called "soft mechanochemistry" introduces mechanochemical syntheses using solids with higher reactivity than anhydrous oxides [16].

To our knowledge, mechanochemical synthesis of spinel zinc stannate has not yet been reported in the literature. Subject of this work is investigation of the influence of grinding conditions in a planetary ball mill on the spinel zinc stannate formation.

2. Experimental

Mixtures of ZnO and SnO_2 powders (Aldrich, p.a.) with a molar ratio ZnO:SnO_2 = 2:1 were mechanically activated by grinding in a planetary ball mill (Fritsch Pulverisette 5). The grinding process was performed in a continuous regime in air during 10, 40, 80 and 160 min at the basic disc rotation speed of 320 rpm and a rotation speed of bowls of 400 rpm. Zirconium oxide balls (approx. 10 mm in diameter) and bowls (500 cm^3) were

---

*Author to whom all correspondence should be addressed.

used with a ball to powder mixture mass ratio of 40:1, and the total weight of powder mixtures of 10 g. Samples were denoted as ZTO-00 to ZTO-160 according to the time of activation.

X-ray diffraction patterns of the milled powder mixtures and of sintered samples were obtained using a Norelco-Philips PW-1050 diffractometer, with a Cu K_α radiation and a step scan mode of 0.02°/0.4 s. Specific surface area of powder samples was measured by the nitrogen gas sorption analyzer (ASAP 2000 Micromeritics) using the BET method.

Differential thermal analysis was performed using a Shimadzu DTA-50 during non-isothermal heating from 20 to 1200°C with a constant heating rate of 10°C/min, in nitrogen atmosphere and the flow rate of 20 ml/min. Relative shrinkage of samples obtained by uniaxial pressing of activated powders was followed by sensitive dilatometer (Bähr Gerätebau GmbH Typ 702s) during non-isothermal heating in air up to 1200°C with a constant heating rate of 10°C/min. Isothermal sintering experiments were performed at 900 and 1200°C for 2 h in a Lenton furnace LTF 16B in air.

3. Results and discussion

Mechanical activation induces physico-chemical changes in a material, which have a significant influence on its properties and hence their application. It was determined that starting powders have specific surface area of 7.33 (ZnO) and 9.01 m^2/g (SnO_2), and with a presumption of a spherical shape, the calculated equivalent diameter of powder particles is about 145 (ZnO) and 95 nm (SnO_2). BET surface area of powder mixtures shows continuous decrease (7.38, 6.84, 3.75 and 3.06 m^2/g for ZTO-00, ZTO-10, ZTO-40, and ZTO-80 samples, respectively). The decreased surface area points to the agglomeration during grinding, and probably due to better sinterability of very fine ZnO particles in the mixture, as already reported in the literature [1].

Fig. 1 shows XRD patterns of ZTO powder mixtures, the initial and those subjected to mechanical activation. Starting powder mixture exhibits sharp peaks of hexagonal ZnO (JCPDS PDF 36-1451) and tetragonal SnO_2 (JCPDS PDF 41-1445). After 10 min of grinding, all sharp peaks of mixed oxides have vanished, the strongest peaks were broadened and the their intensity significantly decreased. Broadening of diffraction peaks indicates that a significant refinement in crystallite size of the initial oxides have been induced by grinding. Upon 40 min of grinding, new broadened peaks of spinel zinc stannate phase, Zn_2SnO_4 (JCPDS PDF 24-1470), are formed indicating the beginning of mechanochemical reaction in the system. Prolonged grinding (160 min) leads to the formation of zinc stannate as a major phase, with insignificant amount of unreacted initial oxides. Our former investigations on influence of mechanical activation (in a vibro-mill) in this system point to the beginning of the spinel formation at 160 min [17]. The difference in times characteristic of the beginning of mechanochemical reaction can be ascribed to the different energy input of a vibro mill and a planetary mill.

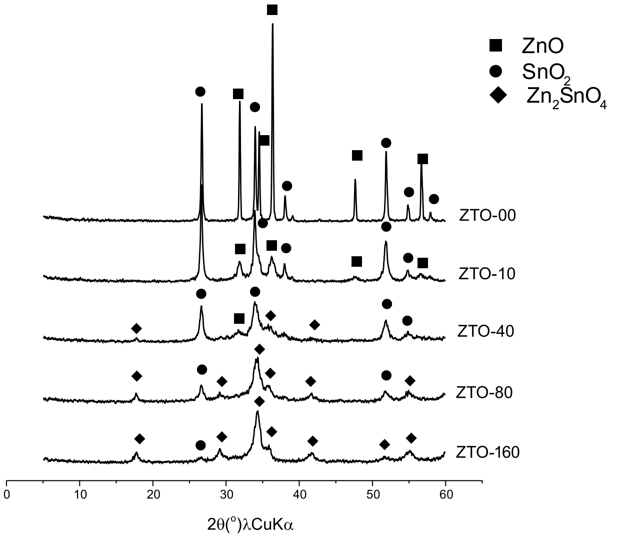

Figure 1 XRD patterns of ZTO powder mixtures as a function of the milling time.

Analysis of microstructural parameters of the strongest peaks of initial oxides and of the formed spinel phase revealed the following. Crystallite size of the ZnO (calculated using Scherrer equation from the broadening of (101) reflection) is reduced from 90 to 15 nm after 10 min grinding, while the reduction of the crystallite size determined from the broadening of the SnO_2 (110) reflection was only from 75 to 65 nm, reaching the value of 14 nm after 160 min. Since zinc oxide is more than six times softer material than tin oxide (microhardness values are 1.5 and 10 GPa for ZnO and SnO_2, respectively [18]), we expected major changes occurring in ZnO. At the same time, the growth of the crystallite size of the spinel was observed with prolongation of the grinding (Table I).

Dilatometric analysis (Fig. 2) and differential thermal analysis of activated powder mixtures (Fig. 3) show thermal behavior of the investigated system.

Dilatometric data show that non-activated mixture exhibits the most intensive shrinkage of all samples, which could be ascribed to the sintering of ZnO in the mixture as a dominant process at lower temperatures (Fig. 2). Intensive shrinkage due to finely dispersed ZnO particles in the ZTO-00 sample starts at about 700°C and as a dominant process overlap expansion due to chemical reaction of spinel formation, which starts at about 1050°C [19]. Zinc stannate was not yet formed after 10 min of grinding, as shown in Fig. 1, and thus spinel formation was initiated after heating at temperatures higher than 900°C (Figs 4 and 5). Sample

TABLE I Crystallite size of the spinel phase formed during grinding and subsequent heat treatment. The crystallite size was calculated from the broadening of the (511) diffraction line

	D (nm)		
Sample	Powder mixture at room temperature	900°C	1200°C
ZTO-40	–	830	1660
ZTO-80	620	995	1660
ZTO-160	88	415	995

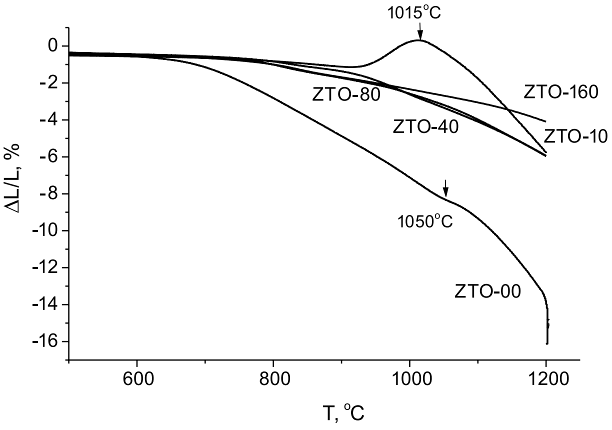

Figure 2 Relative shrinkage of samples as a function of the heating temperature and the milling time.

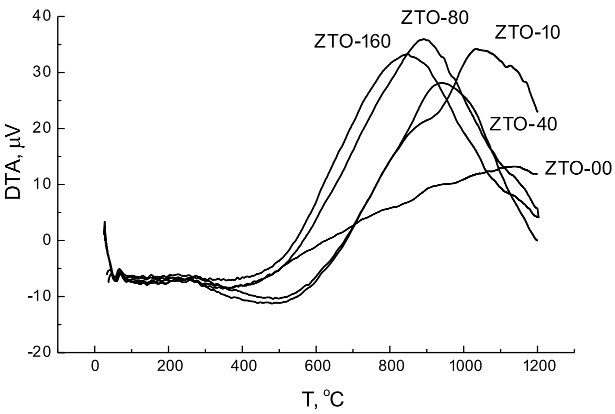

Figure 3 DTA curves of powder mixtures as a function of the milling time.

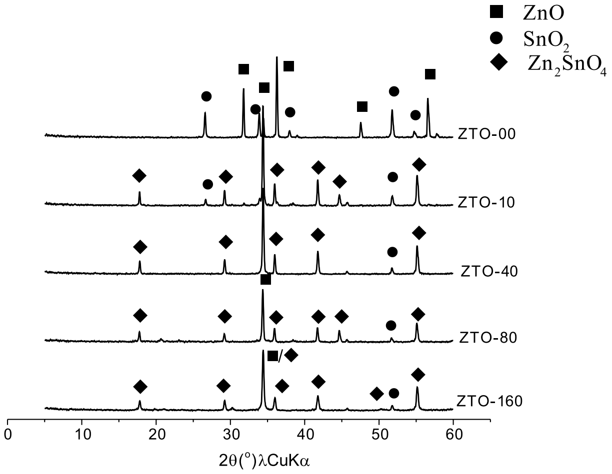

Figure 4 XRD patterns of ZTO samples sintered at 900°C for 2 h as a function of the milling time.

densification takes place simultaneously with the sample expansion, while after the thermal treatment at 900°C, the expansion is the dominant process due to chemical reaction. After sintering at 1015°C, intensive shrinkage starts as the dominant process. Existence of the spinel phase in a form of agglomerates in the system reduced the shrinkage rate with the increase of activation time.

DTA curves of the non-activated sample and mechanically activated mixtures are shown in Fig. 3. It is seen that the DTA curve of the ZTO-10 sample has different shape in respect to other activated samples. Exothermal effect in ZTO-10 sample is a consequence of two processes. First one is due to spinel formation at lower temperatures, and second, is due to crystal growth at higher temperatures. It can also be noticed that the prolonged grinding leads to the shift of the maximum of DTA curves to lower temperatures (see DTA curves for ZTO-40, ZTO-80 and ZTO-160). The observed exothermal effects could be ascribed to the spinel crystal growth occurring with the increase of temperature (Table I).

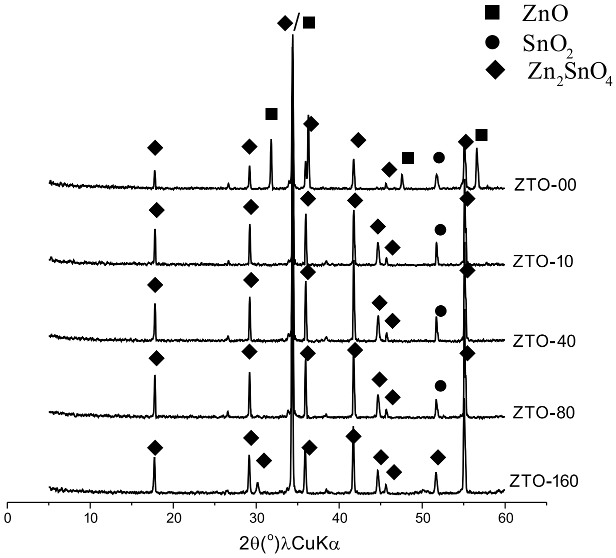

Figure 5 XRD patterns of ZTO samples sintered at 1200°C for 2 h as a function of the milling time.

Since characteristic changes in the system were observed in the temperature range from 900 to 1200°C, X-ray diffraction analysis was performed for the end points of this interval. The spinel formation was observed in ZTO-10 sample sintered at 900°C for 2 h, which is in accordance with dilatometric analysis. The mechanically induced enhancement of the spinel formation at sintering is visible in Fig. 4. Since ZnO is also detected in all activated samples after the thermal treatment at 900°C for 2 h, this can be due to the recrystallization of the amorphous ZnO detected in activated powder mixtures (Fig. 1). When samples were sintered at 1200°C, spinel formation is observed in all samples, and residual oxides are present in all samples except ZTO-160. Thus, the monophased spinel zinc stannate was obtained when powder mixture mechanically activated for 160 min was sintered at 1200°C for 2 h.

4. Conclusions

Formation of spinel zinc stannate (Zn_2SnO_4) and the influence of grinding conditions on the mechanochemical reaction in the 2ZnO:1SnO_2 system were investigated. It was established that the mechanochemical reaction starts after 40 min of grinding in a planetary ball mill. After 160 min of grinding, the spinel phase and insignificant amount of tin oxide are detected in the powder. The spinel formation proceeds slowly for the sample activated for 10 min when sintered at temperatures higher than 900°C, and monophased Zn_2SnO_4 is obtained for sample activated for 160 min and sintered at 1200°C. Based on our present results and preliminary investigations on the mechanochemical synthesis of zinc stannate, two routes for obtaining the zinc stannate spinel-based materials are proposed. First, spinel powder can be synthesized mechanochemically by grinding of a stoichiometric oxide powder mixture in a planetary ball mill for times longer than 160 min, and second, using mechanical activation for more than 10 min and sintering the pre-activated sample at temperatures higher than 900°C.

Acknowledgement

This research was performed within the project No. 1832 entitled "Synthesis of functional materials from the synthesis-structure-properties-application relationship," financed by the Ministry for Science, Technologies and Development of the Republic of Serbia. Authors express their gratitude to Academician M. M. Ristic for helpful suggestions and fruitful discussion. Authors would also like to thank Prof. S. Djuric for X-ray measurements and N. Obradovic for dilatometric analysis.

References

1. W. J. MOON, J. H. YU and G. M. CHOI, *Sens. Act.* B **87** (2002) 464.
2. J. H. YU and G. M. CHOI, *J. Electroceram.* **8** (2002) 249.
3. D. E. SCAIFE, *Sol. Ener.* **25** (1980) 41.
4. J. H. YU and G. M. CHOI, *Sens. Act.* B **27** (2001) 141.
5. W. J. MOON, J. H. YU and G. M. CHOI, *ibid.* **80** (2001) 21.
6. Y. S. SHEN and Z. T. ZHANG, *ibid.* **12** (1993) 5.
7. I. STAMBOLOVA, K. KONSTANTINOV, D. KOVACHEVA, P. PESHEV and T. DONCHEV, *J. Solid State Chem.* **128** (1997) 305.
8. X. WU, T. J. COUTTS and W. P. MULLIGAN, *J. Vac. Sci. Tech.* A **15** (1997) 1057.
9. G. FU, H. CHEN, Z. CHEN, J. ZHANG and H. KOHLER, *Sens. Act.* B **81** (2002) 308.
10. N. HIRATSUKA, H. KOBAYASHI, H. UCHIDA and T. KATSUBE, *J. Ceram. Soc. Japan, Int. Ed.* **104** (1996) 1053.
11. F. BELLIARD, P. A. CONNOR and J. T. S. IRVINE, *Solid State Ionics* **135** (2000) 163.
12. J. FANG, A. HUANG, P. ZHU, N. XU, J. XIE, J. CHI, S. FENG, R. XU and M. G. WU, *Mater. Res. Bull.* **36** (2001) 1391.
13. W. CUN, W. XINMING, Z. JINCAI, M. BIXIAN, S. GUOYING, P. PINGAN and F. JIAMO, *J. Mater. Sci.* **37** (2002) 2989.
14. M. M. RISTIC and S. DJ. MILOSEVIC, "Mechanical Activation of Inorganic Materials" (Serbian Academy of Sciences and Arts, Belgrade, 1998) p. 5.
15. K. TKACOVA, "Mechanical Activation of Minerals" (Elsevier, Amsterdam, 1989) p. 138.
16. M. SENNA, *Solid State Ionics* **63–65** (1993) 3.
17. T. SRECKOVIC, N. NIKOLIC, R. NOVAKOVIC and M. M. RISTIC, *Mater. Eng.* **12** (2001) 33.
18. G. V. SAMSONOV, "The Oxide Handbook" (IFI Plenum, New York, 1982) p. 202.
19. N. NIKOLIC, T. SRECKOVIC and M. M. RISTIC, *J. Eur. Ceram. Soc.* **21** (2001) 2071.

Received 11 September 2003
and accepted 27 February 2004