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The Influence of Mechanical Activation of ZnO and SnO_2 Powder Mixtures on the Obtaining of Zinc Stannate Ceramics

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Abstract

Zinc stannate ceramics has characteristic electrical properties widely used in fabrication of various types of sensors. It is well known that the properties of materials are mostly preparation-dependent and that the structure of ceramic sensor material should be porous. That is just one of the problems that has to be solved, along with the basic one – the obtaining of specific chemical compound, zinc stannate. The subject of this work is the influence of mechanical activation on solid state chemical reaction, *e. g.*, the formation of porous zinc stannate ceramics during different thermal treatments of compact samples obtained from ZnO and SnO_2 powder mixtures activated for various times. Mixture of ZnO and SnO_2 powders (molar ratio 2 : 1) was activated by milling in a vibratory mill with a continual regime in air, for different time periods. The shrinkage behaviour of samples during heating was followed by sensitive dilatometer. X-ray powder diffraction analysis of activated powders and thermally treated samples and SEM analysis were also performed. The main conclusion of the performed analyses is that porous, fine-grained zinc stannate ceramics could be obtained for certain time of activation at much lower temperatures than the ones reported in the literature, with simultaneous acceleration of the chemical reaction.

INTRODUCTION

The beginning of the new century is definitely marked by the necessity for advances in science and technology of new materials including ceramics and thin films that would satisfy the growing demands of materials-related industries involved with electronics, communication, *etc.* Recent advances in electronics are dependent on and closely related to the development of functional materials and their application as electronic components. In the area of well-known oxide materials special attention in the past decade has been paid to some binary systems with promising sensor properties. The requirement for improvement in the properties of these materials can only come from a better understanding of how factors such as composition, processing and structure affect their behaviour.

Zinc stannate (Zn_2SnO_4), one of the compounds which could be synthesized by the conventional ceramic route starting from zinc oxide and tin oxide, has a spinel structure and belongs to the group of conducting oxides possessing improved electro-optical properties [1]. Synthesis of zinc stannate in the form of ceramics [2, 3] or thin films [4, 5] was usually performed in order to explore its sensor properties for the detection of moisture and different combustible gases, but there are only several contributions regarding investigations of the influence of mechanical activation on the formation of zinc stannate ceramics [2, 3].

As it is known, mechanical activation by grinding causes significant changes of physicochemical properties of dispersed oxide powders thus enabling formation of a specific defect structure, besides achievement of very high homogeneity of the powders mixture [6]. Since mechanical activation could enhance powders reactivity and accelerate reaction sintering between oxides due to different mechanisms these facts were used in order to synthesize zinc stannate at lower temperatures and shorter times. The purpose of the present study is to report on the influence of mechanical activation on the obtaining of zinc stannate ceramics from the optimal synthesis parameters viewpoint.

EXPERIMENTAL

Zinc oxide and tin oxide powders (p. a.) were mixtured with the molar ratio of ZnO : SnO_2 = 2 : 1, and then mechanically activated by grinding in a vibratory mill (KHD Humboldt Wedag AG, MH954/3) with a continual regime in air for various time periods (0–160 min). In order to obtain green compacts with approximately the same density for all activated powder mixtures ($0.52-0.56r_t$, where $r_t = 6.42$ g/cm^3 is the theoretical density of zinc stannate [7]) different compaction pressures were applied (75–200 MPa). X-ray diffraction (XRD) patterns of both powders (non-activated and activated) and sintered samples were obtained using a PHILIPS 1820 diffractometer with $CuK_{a1/2}$ radiation and a graphite monochromator, with the step scanning mode of 0.02 °/s. Sintering behaviour of zinc stannate obtained from zinc oxide and tin oxide by the solid state reaction at elevated temperatures was monitored using sensitive dilatometer (Bähr Gerätebau GmbH Typ 702s) during non-isothermal heating in air up to 1200 ℃ with a constant heating rate (10 ℃/min). The morphology of sintered samples was examined by scanning electron microscopy (JSM 5300-JEOL, 30 kV).

RESULTS AND DISCUSSION

Mechanical activation by grinding is a process that proceeds through several stages – from materials destruction to fine grinding and formation of a new surface and various defects. This way a new material is formed with a structure that significantly differs from the starting one. The initial powder mixture contains particles quite different in size (the average particle size of ZnO was 0.230 mm and 0.021 mm for SnO_2). During grinding of the examined ZnO–SnO_2 mixtures a great modification of ZnO particle size distribution occurs thus leading to the formation of a specific microstructure. As was expected, different pressures had to be applied in order to obtained green samples with

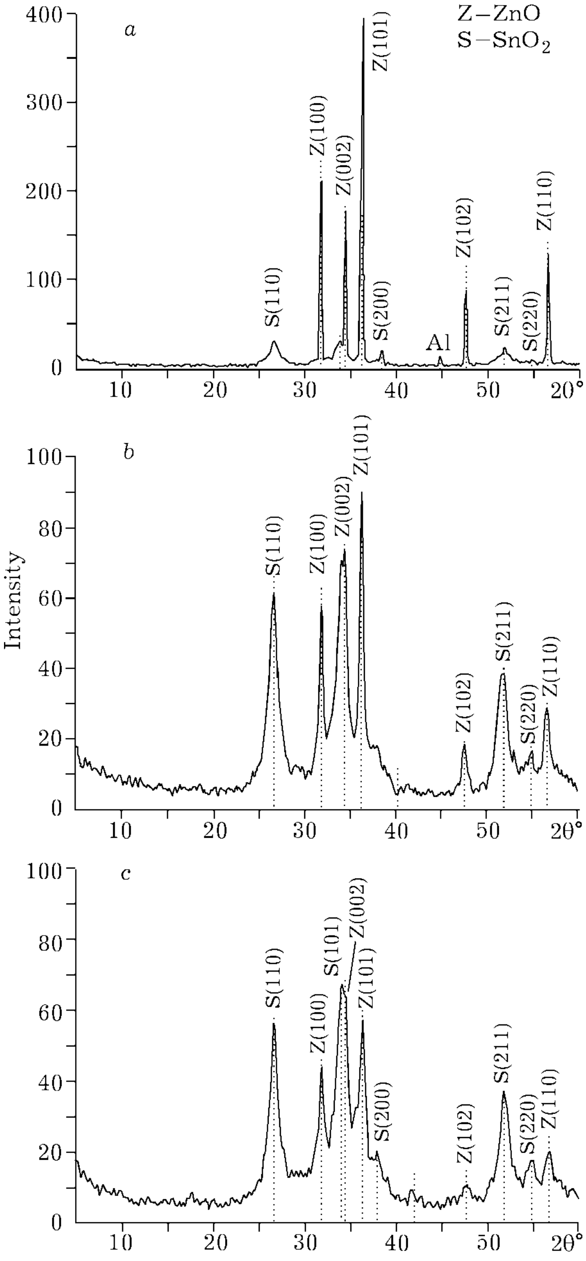

Fig. 1. X-ray diffraction patterns: *a* – starting powder mixture; *b*, *c* – mixtures activated for 80 and 160 min, respectively.

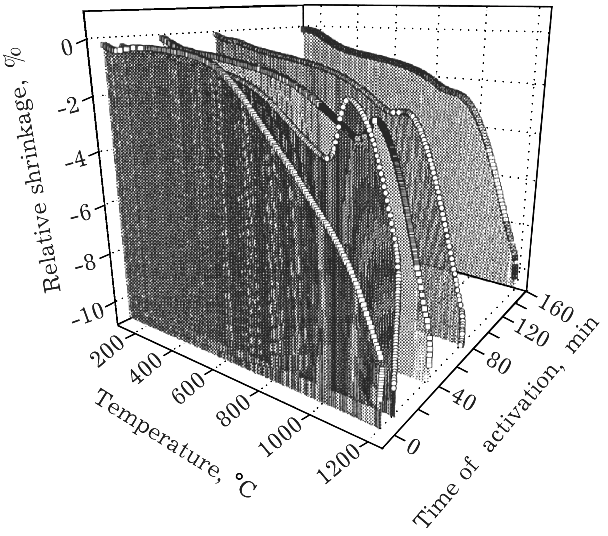

Fig. 2. Relative shrinkage of samples as a function of time of activation and the heating temperature.

approximately the same density because of microstructural changes induced by grinding [8]. The applied pressure required for the compaction of activated powders increased with the increase of time of activation.

Characterization of mechanically activated powders by X-ray diffraction method has been used to examine effects of grinding on crystal structure. Figure 1 shows the X-ray diffraction patterns of the initial mixture of zinc oxide and tin oxide that has been mechanically activated by grinding for various times. The existence of only hexagonal ZnO and tetragonal SnO_2 phases was observed or in other words – there was no evidence of mechanochemical effects, *e. g.* formation of a new phase. The influence of prolonged grinding is manifested by the decrease of intensity and the increase of width, and the change of shape in the observed peaks (mainly those regarding ZnO). As it could be expected and according to a detailed analysis of diffraction data reported in [8], in the $ZnO-SnO_2$ mixture zinc oxide is the one that undergoes more intensive changes during grinding, since zinc oxide is much softer material than tin oxide [9]. A sharp decrease of zinc oxide crystallite size is evident at the beginning of grinding, while crystallite size of tin oxide is practically unchanged. Other microstructural parameters of zinc oxide (dislocations density, microstrains) also change significantly with the increase of activation time [8].

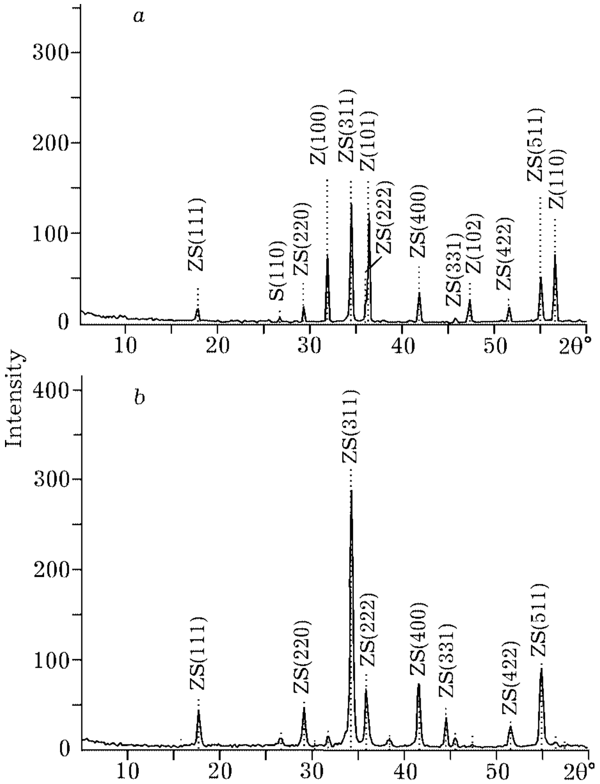

Fig. 3. X-ray diffraction patterns of samples obtained from: *a* – non-activated powder mixture, *b* – mixture activated for 160 min and sintered at 1200 °C for 1 h; ZS – Zn_2SnO_4, Z – ZnO, S – SnO_2.

Results of sintering behavior of the examined $ZnO-SnO_2$ system investigated using sensitive dilatometer are presented in Fig. 2. Differences in dilatometric curves obtained during heating of these samples up to 1200 °C point to the conclusion that activation time significantly affects behaviour of sample during sintering. First of all, the shape of dilatometric curve obtained for non-activated sample is completely different from the ones obtained for activated samples. All samples obtained from activated mixtures of oxides exhibit similar behaviour – there exist two characteristic temperature points, minimal (T_{min}) and maximal temperature (T_{max}), where minimal temperature is denoted as the temperature of the beginning of a chemical reaction between ZnO and SnO_2, since maximal temperature represents the beginning of intensive relative shrinkage of samples (as was discussed in [10]). It is evident that both temperatures quantitatively move towards lower values with the increase of the acti-

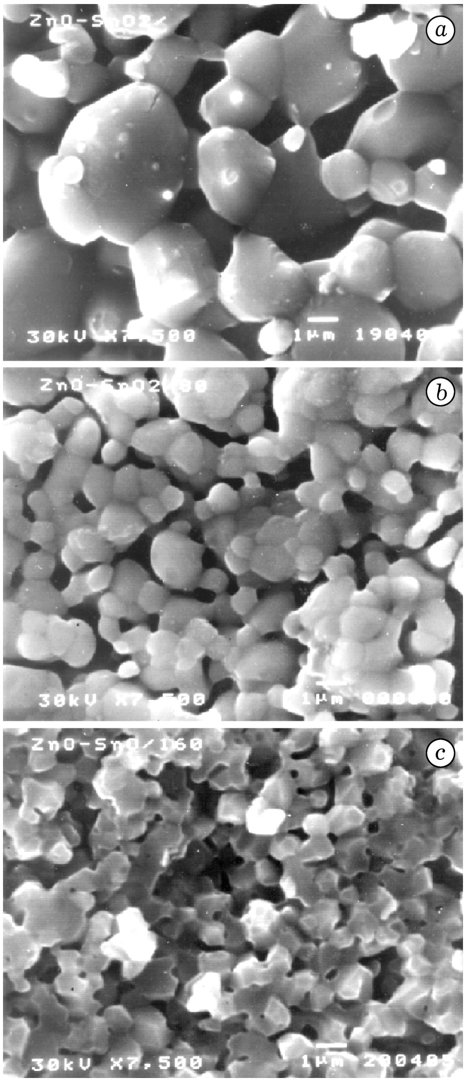

Fig. 4. SEM of the fractured sintered samples obtained from the initial mixture of zinc oxide and tin oxide (*a*), the mixture activated for 80 (*b*) and 160 min (*c*).

vation time (T_{min}, °C: 975 − 945 − 900 − 845; T_{max}: 1050 − 1010 − 965 − 925, for the activation times of 10, 40, 80 and 160 min, respectively). Also, characteristic expansion for spinel formation is smaller when the time of activation is higher, thus implying the increase of reaction rate and possible lowering of sintering temperature at which zinc stannate could be obtained. Previous analysis of the influence of the heating rate on relative shrinkage of samples [11] showed that decrease of the heating rate leads to the increase of relative shrinkage, which should also be taken into account during the optimization of zinc stannate synthesis parameters.

X-ray diffraction patterns of sintered samples are presented in Fig. 3. It was established that zinc stannate spinel is formed during sintering of the initial non-activated mixture, but there still exist both zinc oxide and tin oxide (see Fig. 3, *a*). With the increase of grinding time the reaction of zinc stannate formation is accelerated and only Zn_2SnO_4 peaks were found in sintered sample obtained from powder mixture activated for 160 min (see Fig. 3, *b*). Since other diffraction peaks, which could be associated with either ZnO or SnO_2, were not observed, monophased sintered sample was obtained in the range of experimental error. This proved the fact that system's reactivity strongly depends on the state and structure of initial oxides and their change during grinding.

The sintered ceramic samples, which are constructed from Zn_2SnO_4 spinel grains, were porous as shown in Fig. 4. SEM photographs of fractured sample surfaces suggest that grain size decreased with prolonged grinding. It was expected since particle size of the initial powders was significantly lowered during grinding [8]. The formation of a homogeneous microstructure with a uniform grain and pore size distribution after sintering of activated powder samples is also evident. Application of zinc stannate as a sensor material is closely related with the change of its electrical properties under specific environmental conditions. Smaller particles formed during prolonged grinding promotes solid state reaction leading to the formation of a desired compound (zinc stannate), while large amount of small grains and the raising number of contact surfaces in sintered sample strongly influences electrical properties. Investigation regarding the influence of mechanical activation on electrical properties of zinc stannate will be reported in future works.

CONCLUSION

The subject of this work is the influence of mechanical activation by grinding on the obtaining of zinc stannate. It was established that prolonged grinding and non-isothermal thermal treatment of the zinc oxide − tin oxide mixtures up to 1100 °C enable the suitable condition for the synthesis of fine-grained porous zinc stannate ceramics. Mechanical treatment induces and promotes interaction between zinc oxide and tin oxide *via* sintering leading to the formation of zinc stannate at lower temperatures than the ones reported in the literature.

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