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GAS SENSING PROPERTIES OF NANOCRYSTALLINE METAL OXIDE POWDERS PRODUCED BY THERMAL DECOMPOSITION AND MECHANOCHEMICAL PROCESSING

Dissertation

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Keywords: thermal decomposition, mechanochemical processing, fine metal oxide powders, semiconductor gas sensor.

Abstract

The objective of this research, was the synthesis of $LaFeO_3$ and SnO_2 fine powders for the subsequent preparation of thick film gas sensors.

On producing fine metal oxide powders, often it is not possible to ensure separation of the particles during the synthesis, resulting in the formation of highly agglomerated material. In addition, there are often high synthetic costs associated with the powders obtained by these methods. Thermal decomposition and mechanochemical processing methods were selected to produce fine metal oxide powders.

Thermal decomposition of a heteronuclear complex is a simple and relatively cheap method. Heat treatment of $La[Fe(CN)_6] \cdot 4H_2O$ leads to single-phase perovskite-type $LaFeO_3$ fine powders. Heating in the temperature range 600-750 °C causes fast crystallite growth of slightly agglomerated particles and X-ray diffraction analysis showed only the pattern of orthorhombic transition phase of $LaFeO_3$ particles. A paste for the preparation of the $LaFeO_3$ thick film coating was obtained by mixing of polyvinyl alcohol solution and decomposed powder in a ball mill for 1 h. It was determined that there are two factors important for gas sensing, concentration of surface metal ions $[Fe^{3+}]$, and the concentration of oxygen adsorptive sites $[V_o(..)]$. $LaFeO_{3-\delta}$ thick film with small crystallites, promotes a more rapid NO_2 gas reaction at the surface and allows an equilibrium state to be obtained at 350 °C.

Mechanochemical processing (MCP) is selected as the second, low cost method of manufacturing of fine powders in a conventional ball mill. During milling, deformation, fracture, and welding of powder particles continuously occur. The chemical reactions are activated by the repeated ball-powder collisions. Most of the reports on MCP that have appeared to date, concern the use of high-energy mills. It is shown that it may be possible to produce fine powder particles using a centrifugal mill of the conventional type instead of high-energy one. Nanocrystalline SnO_2 powder was produced by two different chemical reactions. The first reaction, initiated by ball milling, produces water and the second reaction does not produce water. It should be noted that water, produced by the chemical reaction during milling, has a considerable influence on the reactivity of surface. Milling of predetermined stoichiometric amounts of $SnCl_2$ with $Ca(OH)_2$ and K_2CO_3 in an excess of $CaCl_2$ and KCl respectively, resulted in the formation of the desired mass of SnO. After heat treatment and removal of the salt, slightly agglomerated SnO_2 particles were produced with a tetragonal phase, confirmed by X-ray diffraction pattern. A very narrow particle size distribution of the powder is observed.

The response of the $LaFeO_3$ thick film to NO_2 gas is investigated in the temperature range 250-350 °C, where the surface reactions are moderately fast. On exposure to low concentrations of H_2S gas in air in the range 20-50 ppm the SnO_2 film, prepared from anhydrous powder has higher gas response than the film prepared from hydrated powder.

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Preface

This research work was performed in the Laboratory of Electromechanics, Helsinki University of Technology, Finland. The work is related to the synthesis of fine metal powders for the semiconductor gas sensor application by different chemical reactions and milling conditions.

I would like to express gratitude to my supervisor, Professor Tapani Jokinen, Laboratory of Electromechanics, Helsinki University of Technology, for his support and encouraging attitude towards my work. I would also like to thank him for his good advice on writing up the PhD thesis. Special thanks to Professor Asko Niemenmaa, Head of the Laboratory of Electromechanics, for supplying me with a working place and facilities. I would also like to thank him for his interest during the writing of this thesis.

I am grateful that my activities were supported by the scholarship of the Foundation of Helsinki University of Technology. During my stay as a visiting student at the University College Swansea, Wales in 1995-1996, I carried out a study on the tin dioxide based gas catalytic sensors and their response to common types of toxic gases.

In 1998 I was awarded Scandinavia-Japan Foundation Sasakawa scholarship for 6 months to perform research work in Japan. From May to December 1999 I have been a visiting researcher in Ehime University, at the Department of Materials Science and Engineering, where I investigated perovskite-type oxides to determine the feasibility of their utilisation in the detection of NO_2 concentrations in air.

Further I would like to thank Dr. Markku Sundberg, lecturer of the Chemistry Department, University of Helsinki, for our successful collaboration in the field of mechanochemical processing of powders and surface chemistry. He is the co-author of one submitted manuscript for publication.

A special thank should be addressed to Dr. Adrian Taylor of the University of Salford for reading the manuscript and useful discussion.

Finally, I would like to express my gratitude for the financial support provided by the Foundation of Helsinki University of Technology during the period from April, 2001 to April, 2002, for allowing me to complete my postgraduate study and PhD thesis.

Espoo, August 2003

Ülo Kersen

List of symbols and abbreviations

Abbreviations in chemical formulae

A	Large metal, e. g. La in the A site of the perovskite structure
B	Transition metal, e. g. Fe in the B site of perovskite structure
O	Oxygen
M	Metal
x, δ	Amount of oxygen deficiency

Other abbreviations

FTIR	Fourier transform infrared spectroscopy
MCP	Mechanochemical processing
MOCVD	Metal-organic chemical vapour deposition
ppb	Concentration unit (parts per billion)
ppm	Concentration unit (parts per million)
rpm	Rotation speed unit (revolutions per minute)
RT	Room temperature
SEM	Scanning electron microscopy
TD	Thermal decomposition
TG	Thermogravimetry
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

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Contents

List of Publications

The thesis consists of the overview and the following publications.

1. Kersen, Ü. 2001: "Microstructural and surface characterization of solid state sensor based on LaFeO$_{3-\delta}$ oxide for detection of NO$_2$," The Analyst, 126 (8) (2001), pp. 1377-1381.

2. Kersen, Ü. 2002: "H$_2$S-Sensing properties of nanocrystalline SnO$_2$ powder produced by mechanochemical milling," Materials Science Forum, Vols. 386-388 (2002), pp. 633-638.

3. Kersen, Ü. 2002: "The gas-sensing potential of nanocrystalline SnO$_2$ produced by a mechanochemical milling via centrifugal action," Applied Physics A, 75 (2002), pp. 559-563.

4. Kersen, Ü., Sundberg, M. R. 2003: "The reactive surface sites and the H$_2$S sensing potential for the SnO$_2$ produced by a mechanochemical milling," Journal of the Electrochemical Society, 150 (6) (2003), pp. H129-H134.

5. Kersen, Ü. 2003: "The gas-sensing potential of nanocrystalline SnO$_2$ produced by different chemical reactions and milling conditions," Helsinki University of Technology, Laboratory of Electromechanics, Report 70, Espoo 2003, 15 p.

In the following, the publications will be referred with their numbers in brackets, e.g. [1].

The author's contribution

The author has carried out all experiments and written all articles, alone the articles [1-3, 5]. The co-author of the publication [4], Dr. M. R. Sundberg from the University of Helsinki provided support with a useful discussion on writing up the paper.

1 Introduction

1.1 Synthesis of fine metal powders and preparation of sensing films

Fine metal oxide powders for sensing applications have been produced by several methods, including sol-gel processing [Varghese et al. 1999], spray pyrolysis [Korotchenkov et al. 1999], pulsed laser ablation [Zhao et al. 1999], chemical vapour deposition [Brown et al. 2000], sputtering [Rembeza et al. 2000], and thermal decomposition [Traversa et al. 1995, Sadaoka et al. 1998]. The utilization of these methods is often restricted due to high costs or long time scales required for synthesis. To overcome these problems, in this investigation two methods were selected for the production of nanocrystalline oxide powders: thermal decomposition and mechanochemical synthesis.

Nanocrystalline powder offers a significant increase in surface area compared with conventional microcrystalline powders [Williams and Coles 1998]. For gas sensors based on nanosized thick films, where surface reactions are leading to a change in electrical conductance, the grain size is also important in another way. Gas sensor films, prepared from the nanocrystalline powder, offer grain sizes, where the depletion layer has about the same dimensions as the particle radii, and consequently electrical conduction is predominantly grain controlled.

It has been established that when the crystallite size of SnO_2 particles is controlled to less than approximately 10 nm, the sensitivity of the gas sensor is considerably improved [Xu et al. 1991]. When the grains are fully depleted of electrons, very low gas concentrations, much less than 1 ppm, may have a considerable influence on intergrain conduction. It is expected that the crystallite size of SnO_2 particles, produced by mechanochemical processing (MCP), is in the range 10-25 nm.

Thick film gas sensors were prepared by conventional hand coating of a paste, the obtained $LaFeO_3$ and SnO_2 powder, mixed with an α-terpineol-based solvent, respectively, over the Au sensing electrodes on a Al_2O_3 substrate. Finally the substrates were sintered at 700 °C for 1 h in air.

1.2 Thermal decomposition

The conventional method for the preparation of heterometallic ternary oxides, such as $LaFeO_3$ oxide, is the solid-state reaction at high temperatures of the corresponding binary oxides (La_2O_3 and Fe_2O_3). Utilising this method would make it difficult to get single-phase materials, since residual amounts of the starting materials remain in the final product.

Potentially ABO_3 (A = rare earth, and B = transition metal) perovskite type oxides could be prepared by the thermal decomposition (TD) from the corresponding heteronuclear complexes precipitated from aqueous solution. Utilisation of this approach may lead to homogeneous ABO_3 type oxides with a relatively high specific surface area. The method allows the production of trimetallic complexes as a single phase, the decomposition of which leads to the formation of the single-phase of trimetallic perovskite type oxides, containing either two A and one B [Sadaoka et al. 1996], or one A and two B [Sadaoka et al. 1997].

The author of this thesis has demonstrated that fine $LaFeO_3$ powder, with moderately aggregated particles can be synthesized by the TD of a heteronuclear complex $La[Fe(CN)_6] \cdot 4H_2O$ in the temperature range 600-700 °C, having an La/Fe atomic ratio of one. In this work, an investigation of the dependence of microstructural composition of the final products with temperature for TD of the complex, $La[Fe(CN)_6] \cdot 4H_2O$, is reported.

1.3 Mechanochemical processing

Fine powders, which consist of dispersed nanoparticles of 1-100 nm diameter are at present used for a wide range of applications, including nanoelectronics, materials science, biotechnology, energy and solid state gas sensors. These powders have a large volume fraction of atoms at their grain boundaries or particle surfaces. As a result of such microstructure, several properties of nanostructured materials differ from those of bulk or coarse-grained materials [Gleiter 1989]. The synthesis of fine powders by mechanical alloying and milling has been frequently investigated [Schaffer and McCormick 1989, Ding et al. 1996]. Metastable nanocrystalline powders may be obtained in as-milled powder, arising from the particle deformation and fracture, which accompany repeated ball/powder collisions. Plastic deformation of the powder particles initially occurs by the development of shear bands. The shear bands decompose into sub-grains separated by low-angle grain boundaries. With subsequent milling, the sub-grain size reduces and the sub-grains become randomly oriented and separated by high angle boundaries.

Solid state displacement reactions, such as oxidation-reduction and other displacement reactions can occur mechanochemically at RT in a ball mill without any need for external heating. It has been shown that mechanochemical reactions that occur in a continuous manner generally produce a powder, where the particle size decreases to micrometer dimensions, but a nanometer grain size is developed within each particle of the final product phases [Ding et al. 1995]. The MCP also allows the mean particle size to be controlled. Any processing parameter, such as size of the milling vial or time that affects the grain size within the aggregate has an effect on the final particle size.

In this work the synthesis of fine SnO_2 powders by MCP is studied. By using appropriate precursors and chemical reactions, solid state displacement reactions were initiated by ball milling. During processing, each nanoparticle is surrounded with the by-product phase. The subsequent heat treatment resulted in fine particles of the desired phase, dispersed in the matrix of a by-product. Washing with water or pure ethanol was used to remove the soluble by-product phase, resulting in fine powder of SnO_2. The synthesis of fine SnO_2 powders by MCP is reported in publications [2-5].

1.4 Aim of this work

The goal of this research is to present an alternative method to produce fine metal oxide particles with controlled electrical properties for subsequent CO, NO_2 or H_2S gas sensor applications.

The thermal decomposition method has not received much attention in the field of gas sensors due to the fact that powders produced at high temperatures were coarse with a low specific area. One of the aims of this investigation was to study this method for producing pure $LaFeO_3$ powder by TD of a $La[Fe(CN)_6] \cdot 4H_2O$ complex at 700 °C. The decomposition resulted in the formation of moderately agglomerated particles, but with fine microstructure. The use of various temperatures and pressures in the sintering process may cause a decrease in the lattice oxygen on the surface and correspondingly an increase in the number of oxygen vacancies and adsorptive sites.

Mechanochemical processing is selected as the second method for the production of fine metal oxide powders. One of the principal advantages of MCP is its relative simplicity and possibility of obtaining isolated, or slightly agglomerated nanosized particles. Most of the reports in the literature have described the use of either vibratory or planetary mills. It is shown that chemical reactions, which usually occur in the high-energy mill, can be initiated during a short processing time at room temperature in simple centrifugal mill.

1.5 Summary of the results obtained in this work

1) Thermal decomposition of the $La[Fe(CN)_6]\cdot 4H_2O$ complex was achieved at a relatively low temperature of 600 °C, resulting in an orthorhombic $LaFeO_3$ phase of fine particles, with no X-ray diffraction peaks attributable to La_2O_3 or Fe_2O_3.

2) A structural model of nonstoichiometric $LaFeO_{3-\delta}$ oxide is proposed, where the large La^{3+} ion and smaller Fe^{3+} ions are located on the surface of the crystallites. The Fe ions are responsible for the gas sensing properties.

3) The maximum number of adsorption sites formed at the surface of $LaFeO_{3-\delta}$ oxide is determined by the optimal sintering conditions: the largest change in electrical conductivity upon adsorption of NO_2 is observed if the $LaFeO_3$ thick film is sintered in air at 500 °C for 1 h and in nitrogen at 800 °C for 6 h. Variation in the relative gas adsorption capability of the thick film as a function of sintering conditions has not been reported elsewhere.

4) Mechanochemical processing has been widely used in recent years and often utilised for the production of non-agglomerated powder. The author has shown that the milling process itself initially results in the formation of moderately large SnO particles (around 1 μm) covered with a thick layer of $CaCl_2$ (around 0.7 μm).

5) Fine SnO_2 powder can be produced with average crystallite sizes in the range 10-25 nm and a very narrow particle size distribution.

6) If ball milling process produces water, a large number of OH^- groups are formed at the surface, affecting considerably the reactivity of the surface. The gas response tests show that the SnO_2 thick film, prepared from anhydrous powder, has a much higher response to H_2S gas than the SnO_2 thick film, prepared from the hydrated powder.

7) It is proposed that there are, for different reasons, sufficient amounts of $CaCl_2$ and $Ca(OH)_2$ present in the vial during milling. This is a presumption that Ca-OH-Ca bonds are formed, and the subsequent heat treatment transforms these to Sn-O-Sn bonds.

1.6 Contents of the publications

This thesis consists of this overview and five publications. The contents of the publications are briefly summarised in this chapter. Fine metal oxide powders have been produced by two methods: (i) thermal decomposition, described in the publication [1]; and (ii) mechanochemical processing, described in the publications [2-4].

Publication [1]: The heteronuclear complex, $La[Fe(CN)_6]\cdot 4H_2O$, was synthesized at room temperature (RT) by mixing aqueous solutions of equimolar amounts of $La(NO_3)_3\cdot 6H_2O$ and $K_3Fe(CN)_6$ with continuous stirring. The resulting precipitate was collected by filtration and washed with water and then dried in flowing air at 50 °C. The complex was subsequently decomposed at selected temperatures in air in order to obtain perovskite-type $LaFeO_3$ powder. The decomposed samples were prepared by heating the complex up to selected temperatures. As a result, $LaFeO_3$ fine powder with homogeneous particles was obtained.

The surface chemical states and composition of the prepared samples were determined by X-ray photoelectron spectroscopy (XPS). The use of different atmospheres and conditions for sintering allows the modification of the oxygen content of $LaFeO_3$. Sintering in a N_2 gas flow resulted in a much higher degree of $O_{lattice}$ reduction and significantly more oxygen vacancies, compared to sintering in air. In the case of sintering in nitrogen the maximum loss of lattice oxygen is observed at around 800 °C. The concentrations of La^{3+}, Fe^{3+} and oxygen ions were measured to obtain the ratios $[O_{lattice}]/[La+Fe]$, $[O_{ad}+O_{lattice}]/[La+Fe]$ and $[O_{ad}]/[O_{lattice}]$ to characterize the $LaFeO_{3-\delta}$ surface. It is proposed that the derived relationship of $[O_{ad}]/[O_{lattice}]$ may represent the relative gas adsorption capability. In addition to the size of fine powder particles, another two

factors important for gas sensing are the concentration of surface transition metal ions [Fe^{3+}] and the concentration of oxygen adsorptive sites [$V_o(..)$].

A paste for the preparation of the $LaFeO_3$ thick film coating was obtained by mixing of polyvinyl alcohol solution and $LaFeO_3$ powder in a ball mill. Al_2O_3 substrates with comb-type electrodes were coated with this paste and sintered in air, nitrogen and water vapour atmospheres. The influence of sintering temperature on the $LaFeO_{3-\delta}$ surface so obtained was examined in the temperature range 600-1000 °C. The electrical conductivity was measured with an applied voltage of 1.0 V in air and nitrogen dioxide. NO_2 gas response measurements show that at temperatures of 250-350 °C, the surface reactions are moderately fast, but the bulk reaction is much slower as expected.

Publication [2]: Undoped fine SnO_2 powders have been produced by mechanochemical processing, where the milling process was performed at room temperature in a centrifugal mill. The milled composition was subsequently heat treated at 400 °C for 1 h in air. Removal of the $CaCl_2$ by-product was carried out by dissolving it in the distilled water. The washed powder was dried in a furnace at 65 °C. Heat treatment of the milled composition resulted in the formation of both tetragonal and orthorhombic SnO_2 phases, as observed by X-ray diffraction analysis. The fine powder has crystallite sizes in the range from 15 to 20 nm. The powder was characterized by the total pore volume of 0.22 ml/g for a measured particle surface area of 78 m^2/g. The effect of milling conditions on powder properties were investigated, including the milling time and rate, and the mass ratio of the balls and powder. A relationship between the synthesized crystallite size and the amount of salt, $CaCl_2$, added to the starting materials before processing, has been investigated.

La_2O_3-doped SnO_2 thick films were prepared by solution chemistry. The addition of La_2O_3 to SnO_2 was performed by dipping the sintered tin dioxide films in a lanthanum nitrate ($La(NO_3)_3 \cdot 6H_2O$) solution followed by TD at 700 °C for 1 h. Pt wires were attached on the pads of the heater and sensing electrodes by using an Au-paste and heat treatment at higher temperature. The gas response tests were carried out with a PC-based measuring system. The response of the thick-films to H_2S, in the concentration range from 0.5 to 20 ppm in air, revealed that undoped SnO_2 sensors respond to H_2S at a temperature of 250 °C much more strongly than do the La_2O_3-doped SnO_2 sensors.

The results obtained in the present work suggest that the response of the SnO_2 thick film sensor to H_2S gas may be improved by: 1) synthesising powder grains much smaller than 15 nm; 2) using chemical reactions which do not produce water; and 3) washing the powder with pure ethanol, instead of water.

Publication [3]: The synthesis of undoped nanocrystalline SnO_2 powders by mechanochemical processing and the subsequent preparation of SnO_2 thick-films were studied.

A mixture of $SnCl_2$ and $Ca(OH)_2$ was sealed in a non-metallic vial for milling in air. Heat treatment of the milled powder resulted in the formation of tetragonal and orthorhombic SnO_2 phases, which was confirmed by X-ray diffraction analysis. Crystallite sizes in the range from 20 to 30 nm, as determined by XRD measurements, were obtained. The total pore volume was 0.22 mL/g for a measured particle surface area of 37 m^2/g.

During milling the repeated ball-powder collisions induce structural changes and continually regenerate the reacting interfaces. A chemical reaction can take place either during the milling process or in the furnace during the heat treatment stage. A distinct advantage of the MCP method is that the synthesized powder has a large surface area and relatively good porosity, which is important for the application of this material in gas sensors.

In contrast to the high-energy milling often used, the present study shows that it may be possible to obtain powders of nanosized particles using a centrifugal mill of the conventional type. The effect of the milling conditions on powder quality was investigated. One known disadvantage of the high-energy milling is that this results in the contamination of powder and vial. It is shown

that SnO_2 processing is possible in air, i.e. without the requirement of argon or nitrogen atmosphere and no contamination of the powder or vial during milling was observed.

A change in oxygen partial pressure causes a change in the oxygen vacancy concentration in the sintered samples. Heating to temperatures above 500 °C initiates removal of bridging oxygen, leaving oxygen vacancies. In SnO_{2-x}, where x denotes the oxygen deficiency, oxygen vacancies are majority carriers. The SnO_2 thick film sensor's response to H_2S gas can be increased by synthesizing powder grains smaller than 15 nm. It is known that the sensitivity to a gas is significantly increased if the grains are depleted of electrons and the gas response is related to intergrain conduction. The response of the prepared thick-films to H_2S gas in the concentration range from 0.5 to 10 ppm in air was investigated as a function of the sintering conditions. The observed enhanced sensitivity to gas (S=33 upon exposure to 10 ppm of H_2S) can be explained by the increased concentration of oxygen vacancies on the surface.

Publication [4]: The current methods of fabrication of semiconductor SnO_2 gas sensors require the use of fine powder with grain sizes less than 20 nm. After synthesis the powder is mixed with organic solvent to form a paste. In this publication, mechanochemical processing was selected as an alternative method for the production of such fine oxide powders. This method is not time consuming and is of low cost. It is found that the details of powder synthesis have a large influence on the final electrical properties of the gas-sensitive layer.

The starting materials (2.33 g of $SnCl_2$, 0.91 g of $Ca(OH)_2$ and 3.1 g of K_2CO_3) were sealed in a non-metallic vial at RT in air. Heat treatment of milled mixtures at 400 °C resulted in the formation of a tetragonal SnO_2 phase of slightly agglomerated particles. Pure SnO_2 particles were obtained by removal of the $CaCl_2$ or KCl by-product with distilled water or ethanol. The starting materials (2.33 g of $SnCl_2$, 0.91 g of $Ca(OH)_2$, 0.098 g of $Cr(NO_3)_3 \cdot 9H_2O$) were milled to produce the doped SnO_2 phase with Cr distributed on the surface.

After synthesis, the powder is mixed with organic solvent to form a paste. Thick-film gas sensors were prepared by conventional hand coating of a paste, the SnO_2 powder mixed with an α-terpineol or PVA, over the 0.2 mm gap of Au sensing electrodes on a 7×8 mm Al_2O_3 substrate. Finally, the substrates were sintered at 700 °C for 1 h in air.

The infrared spectra of powders synthesized with different milling conditions and chemical reactions are presented. An important finding is that during milling in the presence of water, OH^- groups are formed at the surface. After heat treatment at 400 °C or higher, the OH^- bonds of adjacent grains are probably transformed to Sn-O-Sn bridges. If the chemical reaction initiated by ball milling does not produce water, the FTIR spectrum of the synthesized powder has no surface hydroxide deformations, only a small amount of molecular water shown by the band at 1640 cm^{-1}. Washing the material with ethanol, instead of water, results in the reduction of intensity for the band at 1450 cm^{-1} due to the presence of the bridge bonding Sn-O-Sn. It is concluded in this work that a possible factor, affecting the sensitivity to H_2S gas, is the formation of the strong Sn-O-Sn stretching mode deformation.

Upon exposure to H_2S and CO gas, the SnO_2 film prepared from anhydrous powder, has higher response than the SnO_2 film, prepared from hydrated powder. It is shown that the SnO_2 produced by mechanochemical synthesis can be successfully applied to a H_2S gas sensor.

Publication [5]: Fine SnO_2 powders, used in the preparation of gas sensors, were produced by two different chemical reactions. The first reaction, initiated by ball milling, produces water while the second reaction does not produce water. It should be noted that water present inside the vial or produced by the chemical reaction during milling, has a considerable influence on the milling mechanism. The findings published in [2] show that the milling process itself contributes to the creation of surface hydroxide groups, and after the subsequent heat treatment, even at high temperature, there remains a considerable number of hydroxide groups on the surface of SnO_2 grains.

Most of the reports on MCP that have appeared in the literature concern the use of high-energy mills. The possibility of producing fine powders using a centrifugal mill of the conventional type instead of a high-energy one, has been reported [2-5]. In this publication [5] mill with a high rotation speed (150-200 rpm) was utilised with an enhanced ball-to-powder mass ratio (10:1). A much deeper investigation of milling phase, however, reveals that it is not possible to guarantee separation of all particles during milling, thus resulting in the formation of moderately agglomerated particles.

Mechanochemically synthesized SnO_2 surfaces may have considerably different chemical compositions and reactivities than those prepared by other methods. Surface reactivity can be changed by: 1) milling with a higher speed (200 rpm) and 2) heat treatment of the milled composition at higher temperatures (700 °C). It is concluded that the main sensing mechanism may be explained by the reaction between H_2S and oxygen ions adsorbed on the surface of SnO_2, resulting in an enhanced gas sensitivity for the film, prepared from anhydrous powder.

2 Thermal decomposition

Although perovskite-type oxides of general chemical formula ABO_3 have been extensively studied, they have not been used to a large extent for the preparation of semiconductor gas sensors [Post et al. 1999, Sadaoka et al. 1998]. The majority of research to date has focused on the use of these materials in CO, O_2 and alcohol detection [Kong et al. 1996, Mitsuoka, Post et al. 1993]. $LaFeO_3$ thick films have been found to respond to NO_2 gas [Traversa et al. 1995]. The use of p-type semiconducting oxide powders gives a potential advantage for the detection of oxidizing gases, such as NO_2. Therefore, it seemed to be a reasonable approach to investigate the oxygen-deficient $LaFeO_{3-\delta}$ oxide, considering the possible modification of the ionic crystal structure.

A $LaFeO_3$ nanocrystalline powder with fine and homogeneous particles was synthesized by thermal decomposition of the $La[Fe(CN)_6] \cdot 4H_2O$ complex. The scanning electron micrograph below reveals that the size of the particles, sintered at 800 °C for 1 h in air, is in the range 200-300 nm.
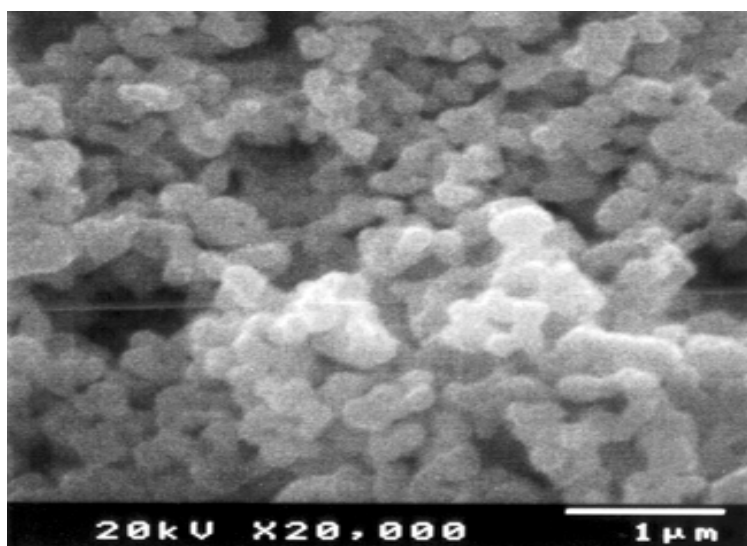

Fig. 1. The microstructure of a $LaFeO_3$ thick film sintered at 800 °C in air for 1 h in air [1].

From the TG data, the weight loss started at about 100 °C and it can be attributed to dehydration of the complex. The intensive weight loss due to exothermic decomposition of the cyanide groups began at around 300 °C, followed by a gradual decrease in weight with a slower rate up to 600 °C. After this, the weight loss remained slow and approximately constant. The XRD pattern showed some diffraction peaks attributed to orthorhombic $LaFeO_3$, together with a broad peak at about 2Θ = 30°, suggesting the existence of a disordered La_2O_3 phase. At temperatures of 700 °C and higher, the XRD pattern of the decomposed complex showed only the peaks of orthorhombic $LaFeO_3$ as seen in Fig. 2.

The use of different atmospheres in the sintering process allows the modification of the oxygen content at the surface of grains. Air, nitrogen and nitrogen with water vapour were used as sintering atmospheres. Two types of oxygen species were found: (a) adsorbed oxygen O_{ad}, which is changed into various surface states; (b) lattice oxygen O_{latt}, which exists as O^{2-} ions. It was shown that sintering in an N_2 gas flow results in a much higher degree of $O_{lattice}$ reduction and more oxygen vacancies, compared to sintering in an air atmosphere. The variation of the intensity of O_{1s} lattice O^{2-} peak in XPS in the temperature range of sintering from 700 to 900 °C in air and nitrogen atmospheres shows that the amount of surface oxygen decreases with increasing sintering temperature [1].
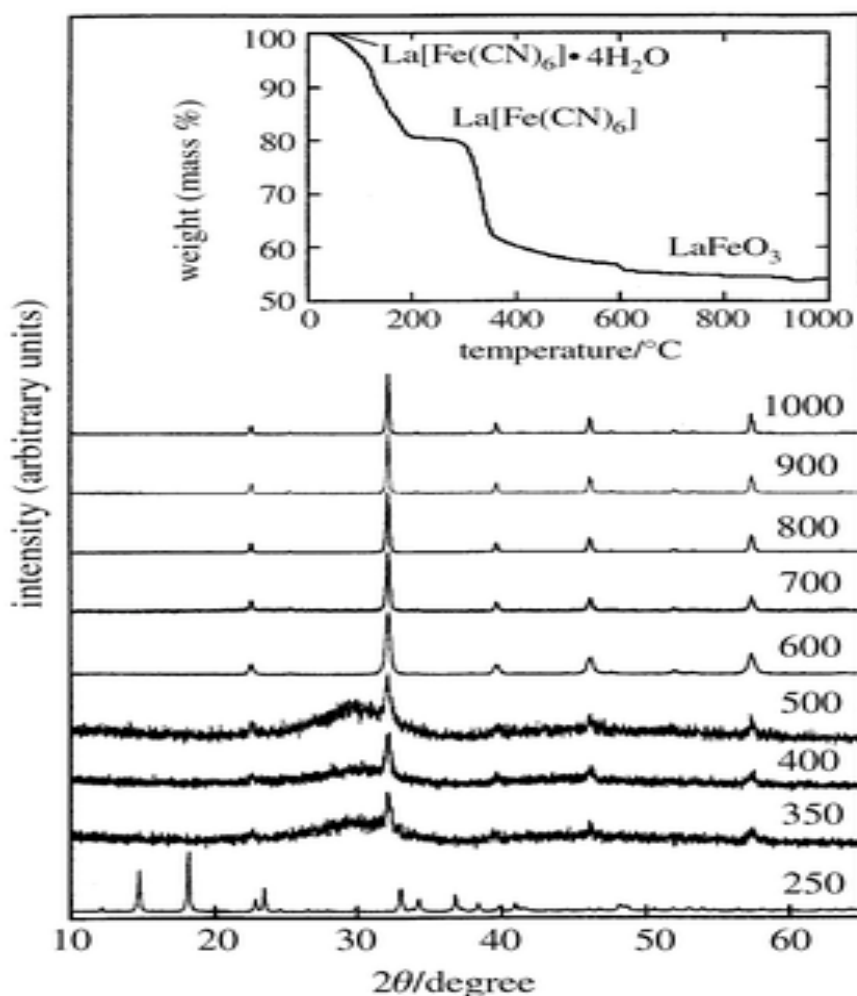

Fig. 2. TG (top) and XRD (bottom) results for the heteronuclear complex heated in air for 1 h at a rate 5 °C/min [1]. Decomposition temperatures are revealed on the right side of the plot.

Surface analysis by XPS makes it possible to determine with sufficient accuracy the atomic ratios of $[O_{lattice}]/[La+Fe]$ and $[O_{ad}+O_{lattice}]/[La+Fe]$, which are dependent on the sintering conditions. The influence of sintering temperature on the $LaFeO_{3-\delta}$ surface was examined in the temperature range 600-1000 °C. In the case of sintering in an N_2 flow, the maximum loss of lattice oxygen is observed above around 800 °C. The ratio $[O_{ad}+O_{lattice}]/[La+Fe]$ shown in the Fig. 3 is nearly constant, showing total charge neutrality at the surface. It is concluded that the ratio of $[O_{ad}]/[O_{lattice}]$ may represent the relative gas adsorption capability of $LaFeO_{3-\delta}$ thick film and can be derived to obtain a relative concentration of surface adsorption sites, which adsorbed oxygen will initially occupy.
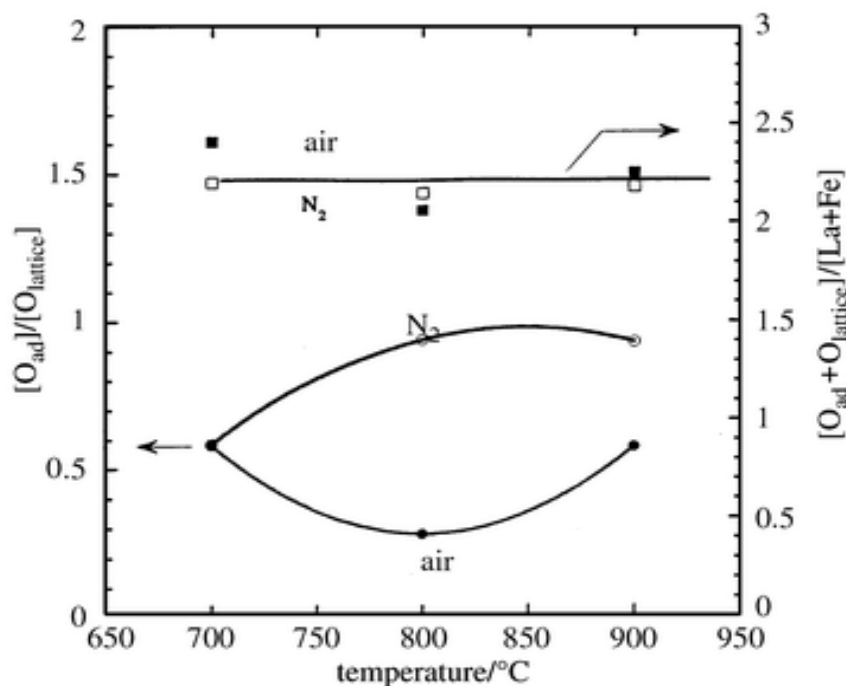

Fig. 3. Variation in the relative adsorption capability of the thick film as a function of sintering conditions [1].

The maximum relative adsorption capability is observed to occur followed sintering above 800 °C in N_2, (Fig. 3). A decrease in gas response may be caused by an increase in the particle size during sintering at temperatures much higher than 850 °C. From the complete surface and bulk characterization of the $LaFeO_{3-\delta}$, it is possible to determine the optimal sintering conditions for the thick film to be prepared.

The gas sensing properties of $LaFeO_3$ thick films, prepared from fine powders, are influenced by the Fe^{3+} concentration and adsorbed oxygen. A fast surface reaction upon exposure to NO_2 gas is observed, but it takes a much longer time to reach an equilibrium state.

3 Mechanochemical processing

Nanocrystalline materials are single-phase or multi-phase materials, the crystal size of which is of the order of a few (typically 1-100) nanometers in at least one dimension. Due to the extremely small size of the grains, a large fraction of the atoms in these materials is located in the grain boundaries, and thus, the material exhibits enhanced physical, mechanical, and magnetic properties (compared to material with a more conventional grain size, i.e. > 1 μm).

Mechanochemical synthesis (also commonly referred to as MCP), of nanocrystalline materials is the general term given to the process of milling of metal (oxide) powders, a process which involves chemical reactions during milling. These reactions can be used to reduce metal oxides and chlorides to pure metals, alloys and compounds [Koch et al. 1983, Tsuzuki et al. 1998].

Fine nanocrystalline powders have been produced by several methods: sol-gel [Vargese et al. 1999], spray pyrolysis [Korotchenkov et al. 1999], pulsed laser ablation [Zhao et al. 1999], chemical vapour deposition [Brown et al. 2000], high frequency sputtering [Traversa et al. 1995] and thermal deposition [Carotta et al. 1997, Sadaoka et al. 1998]. The powders, obtained by these techniques, involving the nucleation of powder particles, are often characterised by a high degree of agglomeration, and thus it is not possible to ensure separation of the particles during the growth stage.

Mechanochemical processing is an alternative method for the production of nanocrystalline materials, where separated (or slightly aggregated) nanoparticles can be synthesized as described in [2-5].

The MCP uses a conventional ball mill, and sometimes a high-energy mill, in which suitable precursor powders are milled to form the desired product. A wide range of materials has been synthesised by MCP, including Fe, ZrO_2, ZnO, ZnS, CeO_2 and SnO_2 [Ding et al. 1995, Ding et al. 1997, Tsuzuki et al. 1997].

3.1 The process of mechanical alloying

Mechanical alloying is a solid-state powder processing technique, involving repeated welding and fracturing of powder particles in a high-energy mill. The process is generally carried out under an inert atmosphere in order to avoid the contamination of the powder. Due to mechanical alloying being a complex process with many variables involved, the mechanism of the process is only poorly understood. However, it is believed to involve powder particles in the ball mill subjected to high-energy collisions, causing the powder particles to be cold-welded together and fractured.

Mechanical alloying can be divided into three stages: at the first stage, powder particles are cold-welded together to form a laminated structure. The chemical composition of the composite particles changes considerably within the particles. At the second stage, the laminated structure is further refined. During this stage dissolution may have started, although chemical composition of the powders is still not homogeneous. Finally, the lamellae become finer and during this stage disappear resulting in a homogeneous chemical composition being achieved for all particles, leading to the formation of a new alloy with a composition corresponding to that of the initial mixture.

For most solid state processes, the initial contact area is fixed and the diffusion rate is limited. It is known that all solid state reactions involve the formation of one or more product phases between the reactants, and that the reaction volume is continually reduced as the reactants (starting materials) become separated during the milling process. Therefore, reaction rates are influenced by the contact area in the initial state and by the diffusion of the starting materials through the product phases. For most solid state processes the initial contact area is fixed and the diffusion rate is limited, hence solid state reactions are temperature dependent.

Depending on the milling conditions, two different reaction kinetics are possible: 1) the reaction can occur in a very small volume during each collision, resulting in a gradual transformation; or 2) if the reaction enthalpy is sufficiently high, a self-propagating combustion reaction can be started. As explained before, the solid state reactions are temperature dependent. This is not the case for mechanical milling-initiated chemical reactions, since a reaction can actually increase with decrease in temperature and a change of phase [Froes et al. 1994].

Many factors influence the powder quality during milling: the type of mill; its size, and weight of the starting materials; velocity, angle and frequency of collisions; ball-to-powder weight ratio;

milling atmosphere; milling time; milling temperature. The actual process of alloying starts with mixing the powders in the mill along with the grinding medium. This mixture is milled for the desired length of time until a steady state is reached. The milled powder is then consolidated into a bulk shape and heat treated to obtain the desired microstructure and properties. Thus, the important components of the mechanical alloying process are the raw materials, the mill, and the process variables.

Different types of high-energy milling equipment are used to produce mechanically alloyed fine powders. Because of the high speed (up to 1200 rpm) of the rotation, the ball mill velocities are high (on the order of 5 m/s) and consequently the force of the ball's impact is considerably high.

Most of the chemical reactions studied in the realm of mechanical alloying, have been displacement reactions of the type:

$$MO + R \rightarrow M + RO \tag{1}$$

where a metal oxide (MO) is reduced by a more reactive metal (reductant, R) to form the metal M. The repeated welding and fracturing of powder particles increase the area of contact between the starting material particles due to a decrease in particle size and allows the surfaces formed to come continually into contact: this permits the reaction to continue without the necessity for diffusion through the product layer. As a result, chemical reactions that normally need high temperatures will take place at lower temperatures during alloying, without any external heating. It should be noted that the high defect densities initiated by mechanical alloying activate the diffusion process. An advantage of using mechanical alloying for the synthesis of fine metal oxide powders is its ability to produce in the solid state bulk quantities of material, using comparatively low cost equipment at RT. It is shown in the publications [2,3] that the chemical reactions can be initiated by the repeated ball-powder collisions in the centrifugal mill of the conventional type to produce the SnO nanoparticles.

In a conventional ball mill increasing the speed of rotation will increase the speed with which the balls move. Above a critical speed, the balls will be pinned to the inner walls of the vial, and do not fall down to exert any impact force. Therefore, the maximum rotation speed should be just below this critical value, so that the balls fall down from the maximum height to produce the maximum collision energy. It was concluded that the rotation speed of 225 rpm equals to the critical value for the mill used in this research.

The minimum grain size achievable by ball milling is determined by [Eckert et al. 1992],

$$D_g = K \cdot t^{-2/3} \tag{2}$$

where D_g is the grain size, t is the time and K is a constant.

The size and shape of the produced powder particles may be precisely determined using direct observations either by scanning electron microscopy for relatively coarse powders or by transmission electron microscopy for fine powders. The crystallite size in the powder particles can be determined using the X-ray peak broadening. Most commonly the crystallite size is determined by measuring the Bragg peak width at half the maximum intensity and using the Scherrer formula

$$D = K \cdot \lambda / B \cdot \cos \Theta \tag{3}$$

where D is the crystallite size, λ is the wavelength of the X-radiation used, B is the width at half the maximum intensity, and Θ is the Bragg angle. K is a constant, depending on the line shape profile. The crystallite sizes obtained indirectly by XRD and directly by electron microscopy may not always exactly match. Whereas the electron microscopy can be used to determine almost any

crystallite size, X-ray peak broadening methods give the most correct results for crystallite sizes in the range of 10-100 nm.

The quality of the synthesized SnO_2 powder was improved by using more input energy for the milling environment, increasing the ball-to-mass weight relationship and the milling time. The estimated SnO_2 crystallite sizes of the final powders (Eq. 3) were in the range of 11.0-12.2 nm. These results are presented in the publication [5].

## 3.2 Ball milling and atmosphere

Mechanochemical processing can be divided into three stages: ball milling, heat treatment and removal of the salt matrix. Most of reactions used or studied in the mechanochemical synthesis, have been displacement reactions, as described before. The repeated ball-powder collisions in the vial of the mill induce structural changes and continually regenerate the reacting interfaces, allowing chemical reactions to occur [McCormick et al. 1998].

It is shown by this work that the activation of chemical reactions by mechanical energy can lead to the production of advanced materials with novel microstructures and enhanced mechanical and electrical properties. Furthermore, solid-state displacement reactions can be started during milling at low temperatures (often at RT).

MCP is a process, where the conversion of mechanical energy into chemical energy is utilized. Milling of the starting materials during of 2-5 h was performed in a centrifugal mill and two chemical reactions were studied.

The Retsch S100 centrifugal mill used in this work is designed for fast loss-free grinding and mixing of many types of soft/medium hard/brittle materials, either dry or in suspension.

The first reaction used is given below

$$SnCl_2(s) + Ca(OH)_2(s) \rightarrow SnO(s) + CaCl_2(s) + H_2O(g) \tag{4}$$
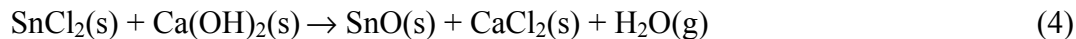
The milling process was performed at RT and in air. It is important to notice that the reaction (Eq. 4) produces water. A ball-to-powder mass ratio of 10:1 was used with a rotation speed of 125 rpm. Removal of the $CaCl_2$ by-product was carried out both with distilled water and with pure ethanol. It should be noted that water vapour present inside the milling vial or produced by the chemical reaction (Eq. 4), has a considerable influence on the milling mechanism.

Fourier transform infrared spectrometry was used for the determination of existing surface species. The FTIR spectra of powders produced by the chemical reaction (Eq. 4) and milled at a moderate speed using the reaction (Eq. 4) are illustrated in Fig. 4 and presented in the publication [4]. A broad absorption band in the range 3750-2500 cm^{-1} is due to the asymmetric hydroxide stretching mode and the band between 820 and 1300 cm^{-1} is assigned to the hydroxide deformation mode. The molecular water deformation mode is located at 1640 cm^{-1}. The band at 1450 cm^{-1} is most probably an overtone of the asymmetric Sn-O-Sn stretching mode of a surface-bridging oxide formed by condensation of adjacent surface hydroxide groups. The SnO_2 stretching vibrations are observed at 625 cm^{-1} and lattice modes of SnO_2 appear at 690 cm^{-1}.

The presence of free water causes a considerable change in the reactivity of the surface. It was found in the present work that washing the heat treated powders with pure ethanol, instead of water, can result in the significant reduction of intensity of the asymmetric Sn-O-Sn bending mode of surface-bridging oxide at 1450 cm^{-1}.

The second reaction used is given below (Eq. 5). The milling conditions are better suited for mixing starting materials during milling, since the reaction does not produce water.
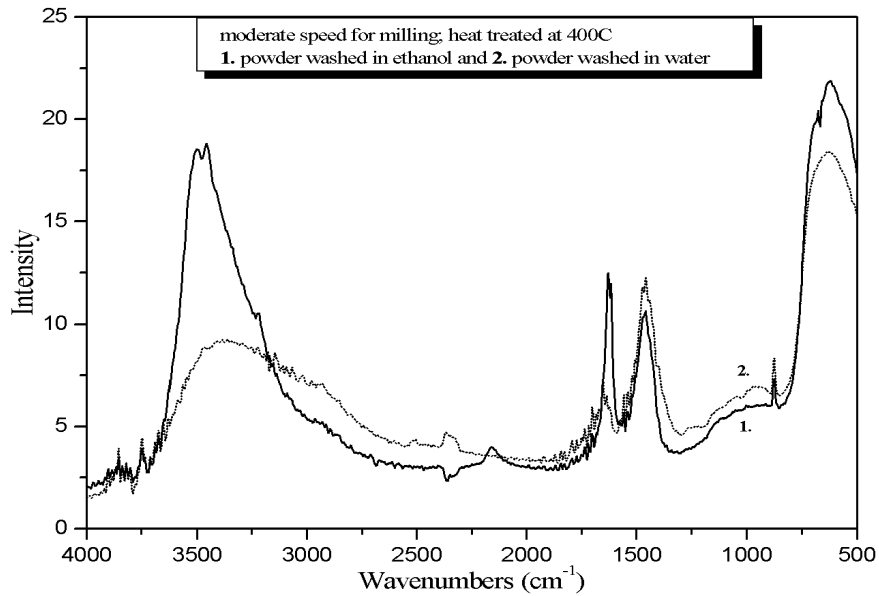
$$SnCl_2(s) + K_2CO_3(s) \rightarrow SnO(s) + 2KCl(s) + CO_2(g) \tag{5}$$
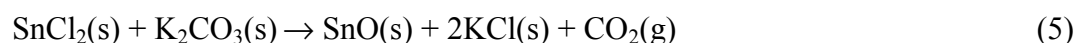
Fig. 4. FTIR spectra of SnO_2 powder milled with moderate speed [4]. Curve 1 shows results for a powder heat treated at 400 °C, and washed with pure ethanol and curve 2 the results for a powder washed with distilled water.

As a result, in this case the surfaces of the SnO grains are not covered with OH groups in great numbers. The FTIR spectra of powders synthesized with different milling conditions and chemical reactions are presented in Fig. 5. The powder produced by the chemical reaction (Eq. 5) and milled
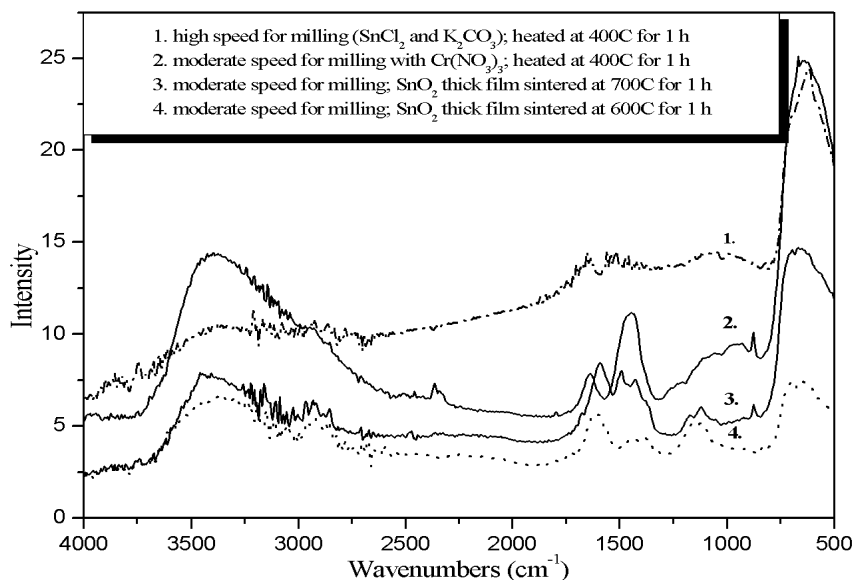

Fig. 5. FTIR spectra of SnO_2 powder milled with high speed [4]. Curve 1 shows the spectrum of the anhydrous powder and curve 2 that of the hydrous powder. Curves 3 and 4 show the spectra of the SnO_2 thick films prepared from these powders.

with moderate speed (curve 1) is characterized by the lowest intensities of adsorption bands, resulting only from the adsorption of water from the gas phase during milling. This is almost a water- and hydroxide-free surface. Curve 2 is the infrared spectrum of SnO_2 powder with Cr_2O_3 distributed on the surface, where the band at 1450 cm^{-1} is increased in intensity. The OH^- groups probably do not stick to the relatively large number of Cr particles on the surface, therefore they are transformed into Sn-O-Sn bonds. Curves 3 and 4 show the spectra of two undoped SnO_2 thick film sensors, sintered at 700 °C and 600 °C, respectively.

An important result was that during milling in the presence of water, produced by the reaction (Eq. 4), the surfaces of grains are covered by the OH^- groups. The FTIR spectra show a band in the range 1632-1640 cm^{-1}, indicating the presence of adsorbed water, and the hydroxide absorption bands in the range 2500-3700 cm^{-1}, for the milled and heat treated SnO_2 powder. It is seen in Fig. 5 that some molecular water and hydroxides remain on the surface at temperatures higher than 600 °C. The intensities of all the adsorption bands are reduced to some extent after high temperature heat treatment. It should be explained here that the powders milled with moderate speed and washed with water have the highest intensities for the asymmetric Sn-O-Sn stretching and hydroxide deformation modes.

Usually the main effect of the milling atmosphere is on the contamination of the powder. If such an effect is expected, the powders are milled in vials that have been either evacuated or filled with inert gas often argon or helium. Nitrogen gas has not been found to react with metal powders and consequently it can not be used to prevent contamination during milling. High purity argon is the most common atmosphere to prevent oxidation or contamination of the vial and powder [Cukrov and Tsuzuki, 2001].

A stoichiometric mixture of $SnCl_2$ and $Ca(OH)_2$ was sealed in the vial under high-purity argon gas and subsequently milled for 3 h in the high-energy mill [Tsuzuki et al. 2000]. After heat treatment of milled mixture at 400 °C, the observed XRD peaks indicated that the chemical reaction had occurred. Nevertheless, it should be noticed that a TEM in the mentioned work reveals that sample is comprised of relatively large, up to 500 nm, aggregates of SnO_2. It is clear that the heat treatment increases the size of the milled particles. Thus, it can be concluded that the synthesis of fine metal oxide particles by MCP, using a high-energy mill sometimes may not produce a suitable microstructure.

In contrast to the high-energy milling described above, the present study shows that it may be possible to obtain SnO_2 powders, using a centrifugal mill of the conventional type. The starting materials were sealed in a non-metal vial in an air atmosphere. Several millings were performed for 2-6 h with a rotation speed in the range 100-200 rpm. The ball-to-powder mass ratio used was 10:1. An advantage of this system is that no contamination of the vial and powder was found during milling and the product SnO_2 powder particles were not agglomerated. The XRD shown in Fig. 6 did not reveal any compounds, which could be related to contamination, as discussed in the publication [2].

A much deeper investigation into the milling phase, however, reveals that it is not possible to guarantee separation of all particles during milling, thus resulting in the formation of slightly agglomerated particles. Processing of starting materials with a rotation speed of 150 rpm causes a formation of SnO particles with mean particle size of 1.5 μm. At the higher rotation speed of 200 rpm, smaller SnO particles are formed; about 1.0 μm with a narrow particle size distribution. After milling a certain time, steady-state equilibrium is attained, when balance is achieved between the rate of welding, which tends to increase the average particle size, and the rate of fracturing, which tends to decrease the average composite particle size. At this stage each particle contains substantially all of the starting materials in the proportion they were mixed together, and the particles reach saturation hardness due to the accumulation of strain energy.
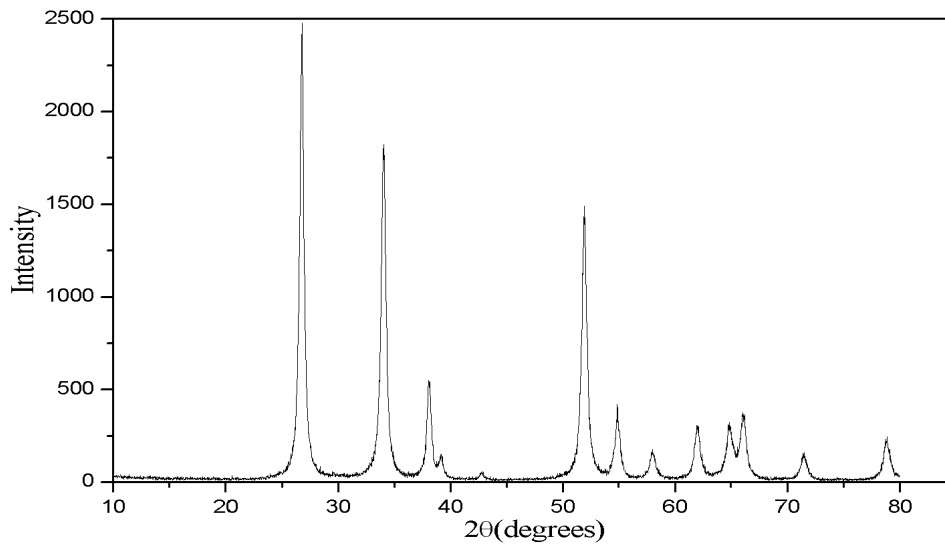
Fig. 6. X-ray diffraction pattern of the synthesized SnO₂ hydrous powder. The milled composition for 1 h was heat treated at 400 °C for 1 h and salt the matrix was removed with water.

The particle size distribution at this stage is narrow, because particles larger than average, are reduced in size at the same rate that those, smaller than average grow through agglomeration of smaller particles. The particle size distribution obtained is shown in the publication [5].

3.3 Heat treatment and removal of the salt by-product

Nanocrystalline metal oxide powders are produced by mechanical milling and subsequent heat treatment in the furnace in air. Chemical reactions between the particles of the starting materials can be initiated during the milling process or subsequent heat treatment, which is necessary in order to complete the metal oxide formation. Finally, removing the salt results in separated, non-agglomerated particles with the composition and size proposed.

The mixture, produced after 3 h ball milling of predetermined amounts of $SnCl_2$ and K_2CO_3, was subsequently heat treated at 400 °C for 1 h in air, resulting in the exothermic reaction,

$$SnO(s) + 1/2(O)_2(g) \rightarrow SnO_2(s) \qquad (6)$$

Removal of the KCl by-product was carried out both with distilled water and with pure ethanol. An XRD pattern of the synthesized powder, after removal of the KCl mass and drying, reveals the tetragonal phase, which is dominant, and together with the orthorhombic phase giving the rise to only two very weak peaks as shown in Fig. 7. It may be concluded that the crystallization has succeeded at this low temperature of 400 °C. Compared to the XRD pattern in Fig. 6, an increase in milling time from 1 h to 3 h results in the decrease in crystallinity that is expected.

Harrison and Guest [1987] have concluded that dehydration of the surface of SnO₂ occurs principally via condensation of adjacent surface hydroxide groups on the (100) plane with secondary condensation on the (101) plane. Hydroxide group condensation on these two planes will lead to the formation of surface Sn-O-Sn bridges. It was concluded in the work [4] that a possible factor, affecting the sensitivity to H₂S gas, is the formation of strong Sn-O-Sn stretching mode deformation. FTIR spectra for the powders produced with different milling conditions and chemical reactions, are presented in the publications [4,5].
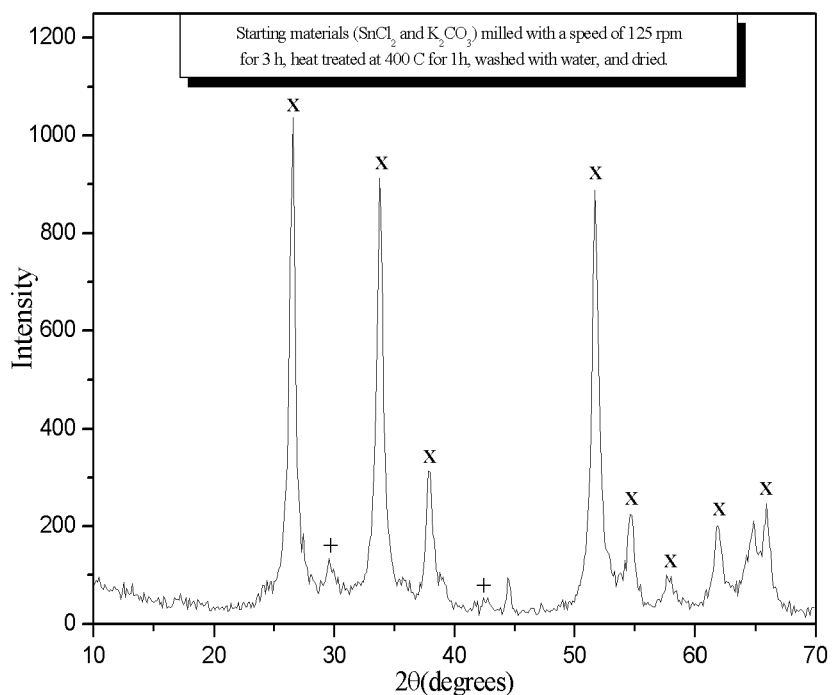
Fig. 7. X-ray diffraction pattern of the synthesized SnO$_2$ anhydrous powder with a typical distribution of the tetragonal (x) and orthorhombic (+) phases [5].

It was suggested that strong oxygen bonds, formed during the dehydration, remain on the surface and thus reduce the number of active sites for gas adsorption. At high speed milling (200 rpm) there is no essential difference between the OH$^-$ band intensities, whether the heat treated composition was washed by water or ethanol. The differences can be found in the intensity of the band at 1450 cm^{-1} as presented in Fig. 8. The sharp peak at 890 cm^{-1} can be attributed to a surface hydroxide deformation band.
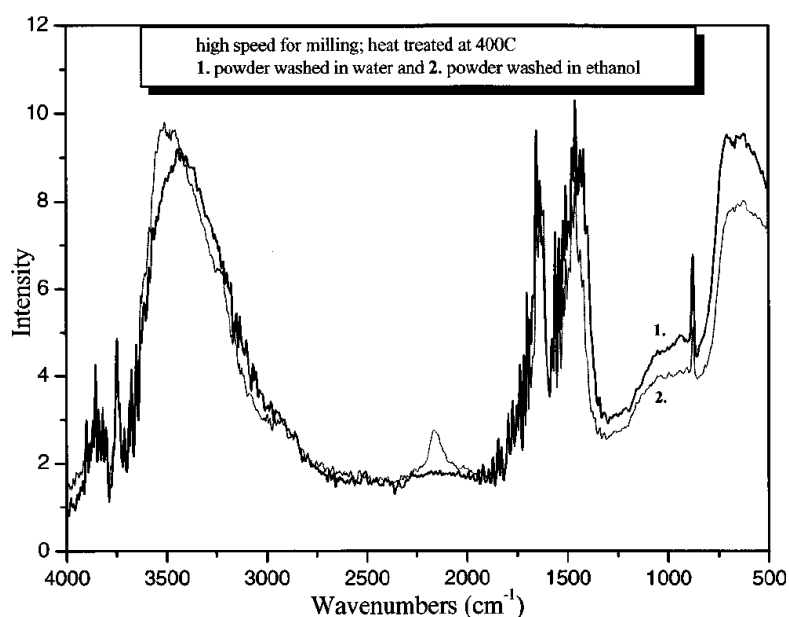

Fig. 8. FTIR spectra of SnO$_2$ powder milled with high speed [4]. For curve 1 the powder was heat treated at 400 °C and washed with distilled water, while for curve 2 the powder was washed with pure ethanol.

4 Gas sensors

4.1 Perovskite-type thick film sensors

$LaFeO_3$ oxide is typically a p-type semiconductor; but the oxide may have a highly nonstoichiometric composition, which leads to n-type electronic conduction when the oxygen content is substoichiometric. For the gas sensor applications, the preparation of controlled porous structure is important. The control of the microstructure of final powder can be obtained using fine homogeneous powders as starting materials.

ABO_3 perovskite-type oxides are promising materials for use as fuel cells, catalysts, materials for electrodes, as well as, for gas sensors. Thick and thin films of $LaFeO_3$ have been studied by several authors [Matsuura et al. 1993, Traversa et al. 1995]. These works have shown a noticeable response to NO_2 gas in the concentration range 1-10 ppm.

Fine $SmFeO_3$ powders, prepared by the thermal decomposition at 700 °C of the corresponding hexacyanocomplex $Sm[Fe(CN)_6]\cdot4H_2O$ are studied in the work of Carotta et al. (1998). The powders produced were used for the preparation of thick films and screen-printed on alumina substrates with comb-type Au electrodes. The author of this thesis does not agree that the films prepared in the mentioned work are highly porous and that sintering did not considerably change the size of the grains. There are two reasons for this disagreement: 1) the prepared NO_2 sensor is not highly sensitive and 2) no equilibrium state is observed upon gas exposure. It is very probable that the thick film fabricated is not sufficiently porous, therefore the rate of diffusion of gas into the film is slow. It is concluded by the author of this thesis that $SmFeO_3$ thick films prepared by this way, are not promising materials for use in gas sensor devices.

In this research, initially $LaFeO_3$ powder was obtained by a solid-state reaction. A 1:1 mixture of a 1:1 ratio of La_2O_3 and Fe_2O_3 was prepared by ball milling for 48 h and sintered at different temperatures. Heat treatment at 800 °C or higher led to the formation of pure perovskite-type oxide, but containing residual amounts of the starting oxides, La_2O_3 and Fe_2O_3. Powder obtained in this way had lost a fine microstructure and a high surface area, if compared to the powder obtained by thermal decomposition of a heteronuclear complex, $La[Fe(CN)_6]\cdot4H_2O$, in the temperature range 600-700 °C. In the latter case the formation of more pure fine powder was observed, but with slightly agglomerated structure. These agglomerations are reduced in the size to some extent after ball milling of the powder for 1 h. However, the measured particle surface area of $LaFeO_3$ powder, decomposed at 700 °C, was not high, but only around 10 m^2/g.

The sensitivity of $LaFeO_3$ to NO_2 gas can be considerably improved if it is possible to determine the optimal sintering conditions [1]. Sintering at 500 °C for 1 h in air and in nitrogen gas flow at 800 °C for 6 h are found to be the optimal sintering conditions for the film, with respect to a maximum concentration of ions $[Fe^{3+}]$ and oxygen vacancies $[V_o(..)]$ on the surface. The sensitivity of a thick $LaFeO_{3-\delta}$ film treated by optimal sintering conditions is shown in Fig. 9.

A paste for the preparation of the $LaFeO_3$ thick film coating was obtained by mixing five drops of polyvinyl alcohol solution and 0.1 g of thermally decomposed powder. Using the optimal sintering conditions introduced above, an enhanced sensitivity to NO_2 gas can be achieved due to the formed surface transition metal ions and oxygen vacancies.
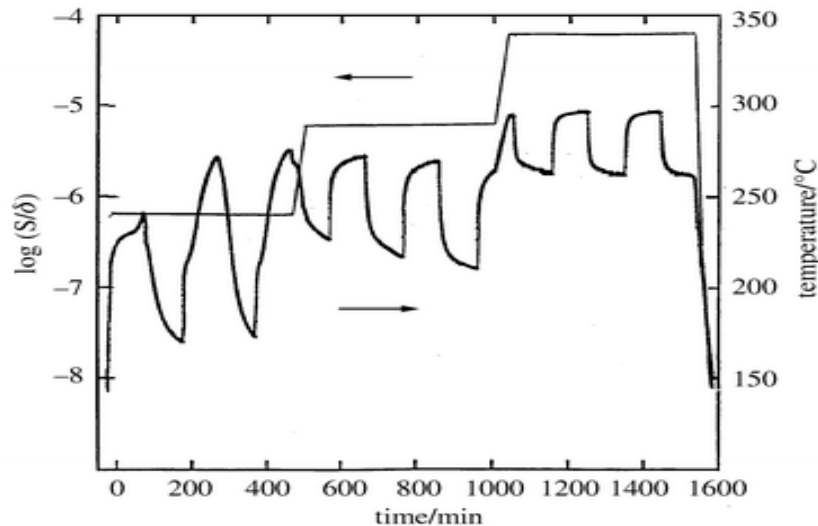
Fig. 9. Dependence of the conductivity on the operating temperature in alternating O_2 and 10 ppm NO_2 atmospheres for an $LaFeO_{3-\delta}$ thick film sintered in air at 500 °C for 1 h and in N_2 at 800 °C for 6 h [1].

4.2 SnO$_2$ thick film sensors

The conduction of SnO_2 in air, heated in the temperature range 100-450 °C, is influenced by the chemisorption of oxygen and of water vapour on the surface of the SnO_2 grains, associated with electron abstraction from the conduction band [Moseley et al. 1991]. This process creates an electron depleted surface region, which represents a barrier to electrical conduction between the SnO_2 grains. A combustible gas can react with the surface oxygen species, permitting electrons to be re-introduced to the surface region, which leads to a decrease in the depth of the space charge layer. It is important that the sensor is prepared in such a way that surface phenomena dominates. This is the case for nanocrystalline porous and thin layers, where the measured effects are large enough to detect low concentrations of gas.

Only two studies seem to have been published to date on SnO_2 thick or thin film gas sensors prepared from powders by MCP [Cukrov and McCormick 2001, Cukrov and Tsuzuki, 2001].

SnO_2 nanoparticles, averaging 24 nm, were produced by MCP in the work of Cukrov and McCormick (2001). The powder consisted of separated tin dioxide nanoparticles with a tetragonal phase and was examined by XPS.

The synthesis of fine SnO_2 powders by mechanochemical processing for gas sensing applications is reported in the publications [2-5]. The effect of milling conditions on powder properties were studied, including the milling time, rotation speed, the mass ratio of the balls and powder. It is reported in the publication [2] that the important factor associated with the sensing mechanism of a prepared SnO_2 thick film is the grain size. Fine powders can be successfully used for the preparation of semiconductor gas sensors if they have a crystallite (grain) size of less than 15 nm. Crystallite sizes of produced fine powders in the range from 10 to 25 nm were determined from X-ray diffraction line broadening in this research work.

Thick-film gas sensors were prepared by conventional hand coating of a paste, the SnO_2 powder mixed with an α-terpineol-based solvent, over the 0.2 mm gap of Au sensing electrodes on a 7×8 mm Al_2O_3 substrate [2]. Subsequently these substrates were sintered at 700 °C for 1 h in air. Pt wires were attached to the pads of the heater and sensing electrodes by using an Au-paste and heat treatment. The H_2S and CO gas response tests were carried out with a PC-controlled measuring system. Sensors to be tested were placed in a measuring chamber of about 0.5 dm^3 in volume.

Optimum detection temperatures were determined and thick-film sensors maintained at this fixed temperature were exposed to varying test gas concentrations of H_2S (in the range 1-50 ppm) and CO (in the range 20-100 ppm), using a gas flow controller unit with an air flow rate of 0.5 dm^3/min. Response, S, to gas is defined as

$$S = R(air) / R(g) \qquad (7)$$

where R(air) is the sensor resistance in clean air and R(g) is the resistance in the test gas. The prepared thick film sensors revealed moderately high response and recovery times. As it can be seen in Fig. 10 the response time (at the level of 0.9) is about 10 min. The maximum responses to H_2S gas were achieved, with S = 300 and S = 30, upon exposure to 20 and 10 ppm of H_2S gas respectively. The response time of an SnO_2 sensor that was doped with 1.0 at % La_2O_3 was not so high (S = 30). Very likely neither the undoped nor the doped sensors have sufficient porosity and subsequently the gas response time is rather long.
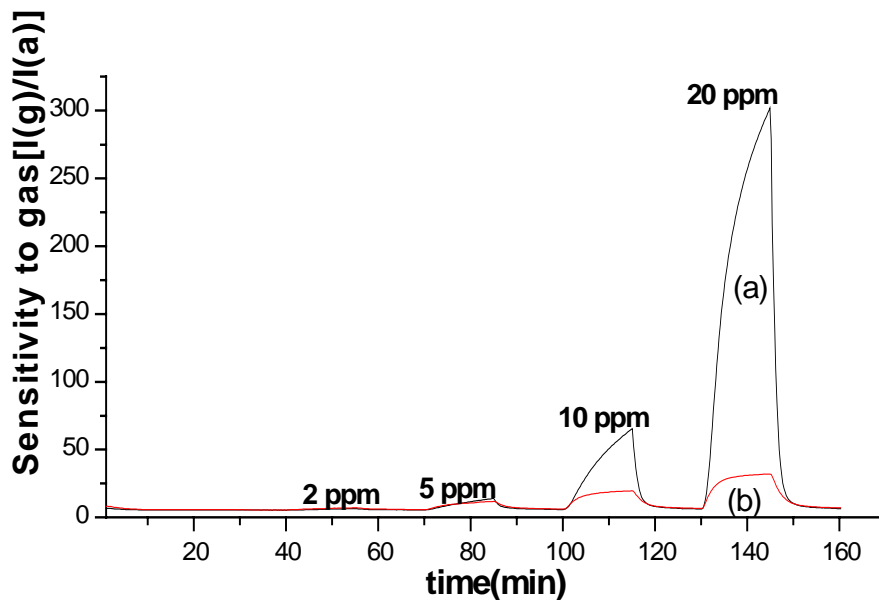

Fig. 10. Dynamic response of undoped SnO_2 (a), and 1.0 at % La_2O_3-doped SnO_2 (b) thick films to increasing H_2S concentrations in air [2].

An investigation of the milling phase shows that it is not possible to guarantee separation of all the particles during milling, thus resulting in the formation of agglomerated particles. This is clearly a disadvantage for the mechanochemical processing method.

If ball milling does produce water, the OH^- groups are formed at the surface in great numbers, contributing considerably the reactivity of surface. It was found in the present work that by an appropriate selection of milling conditions and chemical reaction, it is possible to reduce the intensity of the antisymmetric Sn-O-Sn modes of surface-bridging oxide at 1450 cm^{-1}. This important result is reported in the publications [4-5].

In the further study, the response of the prepared thick films to H_2S gas in the concentration range 0.5-10 ppm in air was investigated as a function of the preparative conditions [3]. Thick film gas sensors were prepared by conventional hand coating of a paste, the SnO_2 powder mixed with a terpineol-based solvent, over the Au sensing electrodes on an Al_2O_3 substrate. These substrates

were sintered in the temperature range 500-700 °C for 1 h in air and one thick film was sintered at 700 °C for 1 h in a N_2 gas flow.

Sintering at temperatures above 500 °C in a reducing gas flow may remove oxygen on the surface and create corresponding oxygen vacancies [Gillan et al. 1995]. Good sensitivity and the response to H_2S gas for the concentrations below 1 ppm in Fig. 11 are due to the increased concentration of oxygen vacancies. These defects are main carriers of SnO_{2-x} thick film, where x denotes the oxygen deficiency.
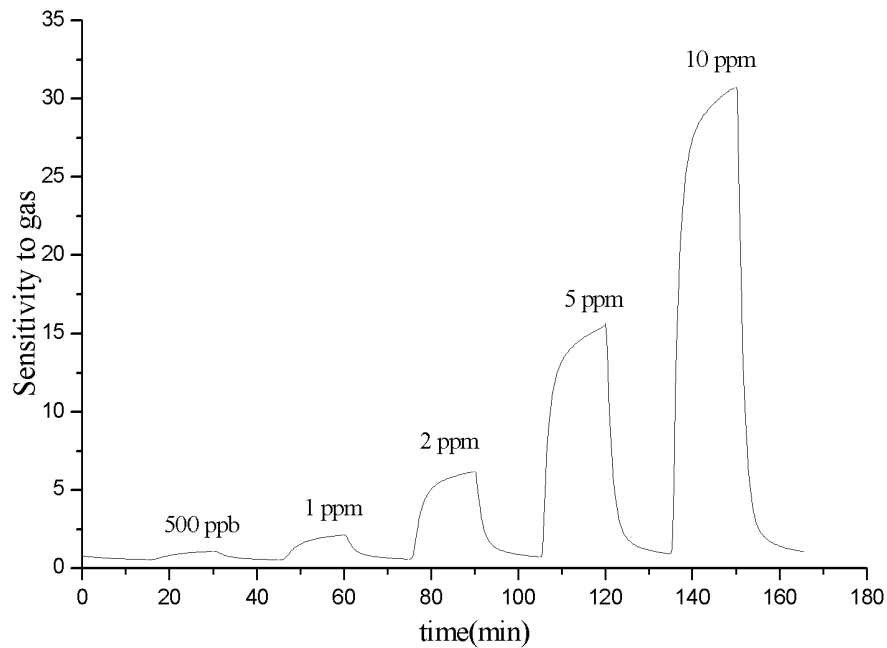
Fig. 11. Dynamic response of SnO_2 thick film sintered at 700 °C in an N_2 atmosphere for 0.5 h to increasing H_2S concentrations in air [3]. An air flow rate was kept at 0.5 dm^3/min.

As mentioned before most of the methods producing the fine powders are basically related to the chemical processing: co-precipitation, sol-gel or MO-CVD. Very few reports are found where nanosized powders as gas sensing materials are produced using the method of mechanical alloying [Tan et al. 2000, Jiang et al. 1997].

Structural features of fine powders in relationship with the high-energy ball milling and the sensing properties of nanocrystalline $xSnO_2$-(1-x) α-Fe_2O_3 ethanol sensors were studied in the work of Tan et al. (2000). Non-equilibrium fine $xSnO_2$-(1-x) α-Fe_2O_3 powders have been prepared by high-energy milling. Good sensitivity to gas, as shown by thick films, is explained by a non-equilibrium model, where the oxygen dangling bonds at the particle surfaces give rise to the increase in sensitivity. The sensitivity to 1000 ppm of ethanol gas was high, but this work does not contain any dynamic gas response plots, therefore it is not possible to determine the quality of prepared sensors. A clear disadvantage is that milling times to mix the starting materials were too long, over 80 hours.

An important feature of mechanochemical processing is that after milling the composition may have high surface charge due to a large number of surface OH^- groups formed on the surface. Thus, the reactivity of surface depends on the energy input introduced into the system and the type of chemical reaction to be used at the first stage of mechanochemical processing.

The conclusions, represented in the publications [2-3], were taken into consideration in a subsequent study and the results are shown in the publications [4-5]. Sensors were prepared from the hydrated and anhydrous powders. Optimum detection temperatures were determined, and thick-film sensors maintained at this fixed temperature were exposed to varying test gas concentrations of H_2S and CO. The SnO_2 crystallite size, determined using Scherrer's equation, was in the range 10-20 nm dependent on the different milling conditions. A measured specific surface area of 79 m^2/g for the powder produced by mechanochemical processing confirms a substantial increase in surface area.

The response and recovery times of sensors made from the powders depend on the operating temperature, both being slow at low temperatures, and fast at higher temperature. An operating temperature of about 225-250 °C was found to give the maximum sensitivity to H_2S gas. The increase of the conductivity in the presence of H_2S (Fig. 12) may be explained by the reaction between H_2S and oxygen ions on the surface of SnO_2 grains

$$H_2S + 3O^{2-} \rightarrow SO_2 + H_2O + 6e^- \tag{8}$$
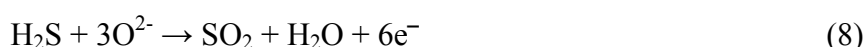
According to this reaction, the interaction of H_2S with adsorbed $3O^{2-}$ ions results in the injection of electrons into the depletion layer of SnO_2 grains.

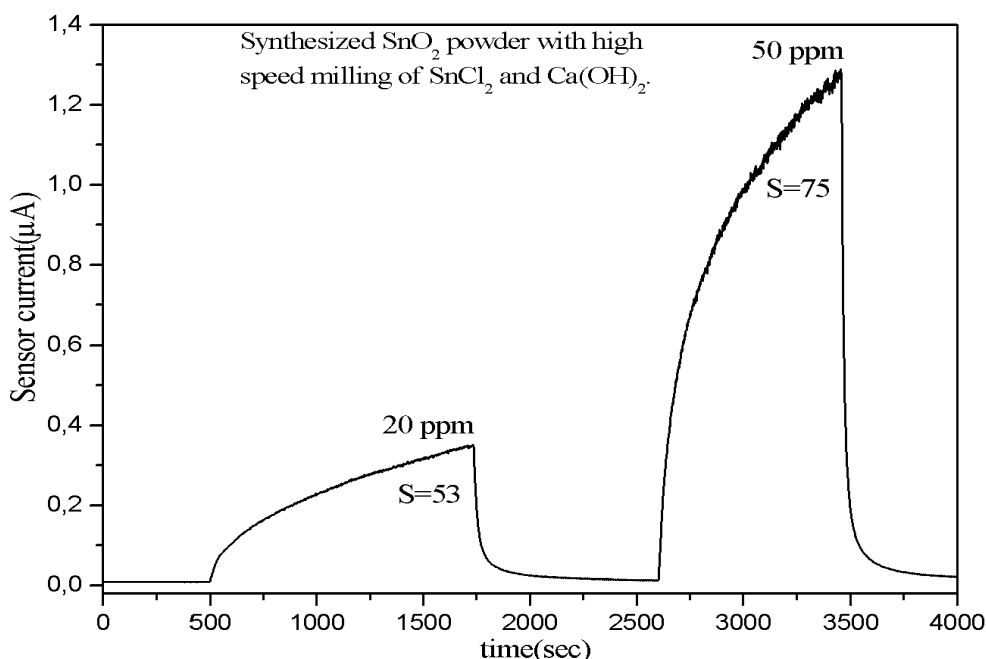**Fig. 12.** Dynamic response of an SnO_2 thick film sintered at 700 °C in air for 1 h to increasing H_2S concentrations in air. An air flow rate is maintained at 0.5 dm^3/min [5].

If the chemical reaction during milling does not produce water, the FTIR spectra for the powders do not reveal great numbers of surface OH^- groups. Most of the surface oxygen ions are located near the tin ions on the surface. A comparison of the sensitivity to H_2S and CO gas for the different types of SnO_2 sensors has been performed in order to confirm the proposed gas sensing mechanism. When the powder was obtained using milling at moderate speed with the chemical

reaction without producing water, the resulting thick film had a more distinct response to test gas as shown in the publication [5]. A possible explanation for this could be that powders manufactured with high and very high milling speeds have greater surface charge due to a large number of surface OH^- groups. During heat treatment, however, most of OH^- groups are transformed into strong surface Sn-O-Sn bonds, which are probably not involved in gas adsorption.

Thus, the main sensing mechanism may be explained by the reaction between H_2S and oxygen ions, adsorbed on the surface of SnO_2, resulting in the enhanced gas response for the film prepared from anhydrous powder good response upon exposure to H_2S gas (Fig.13). It is clear that the fast response to H_2S gas of the SnO_2 film prepared from anhydrous powder is attributed to the chemical sensing mechanism which considers only the gas reaction with the surface adsorbed oxygen ions and OH^- groups do not contribute the gas sensing mechanism.
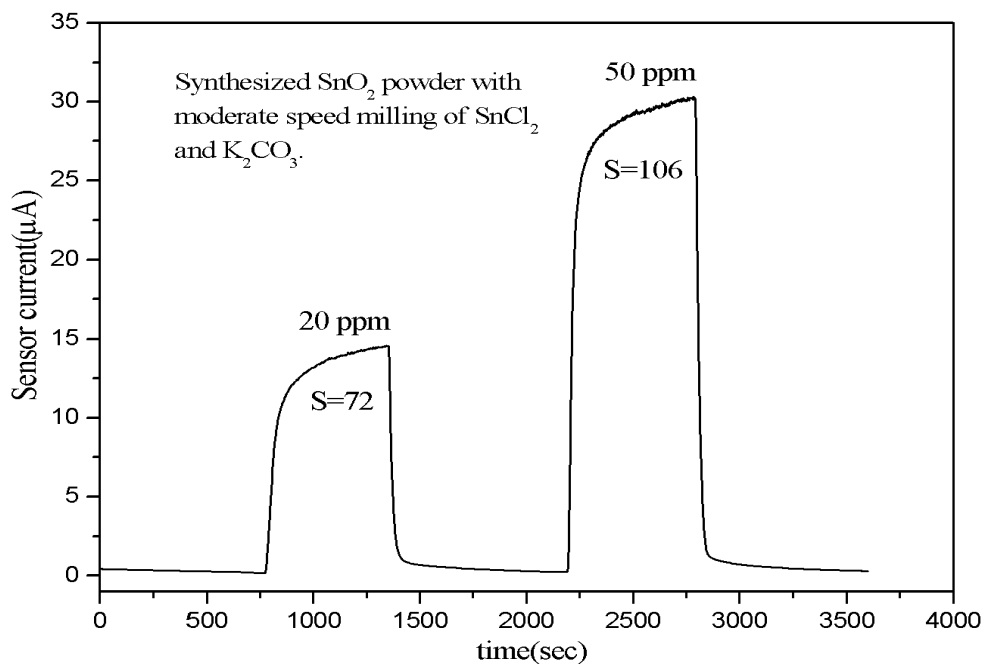

Fig. 13. Dynamic response of an SnO_2 thick film sintered at 700 °C in air for 1 h to increasing H_2S concentrations in air. An air flow rate is maintained at 0.5 dm^3/min [5].

5 Conclusions

The thermal decomposition of the La[Fe(CN)$_6$]·4H$_2$O heteronuclear complex in the temperature range 600-1000 °C resulted in the formation of a nanocrystalline single phase of orthorhombic LaFeO$_3$. At temperatures higher than 700 °C no X-ray diffraction peaks attributable to La$_2$O$_3$ or Fe$_2$O$_3$, were found, thus confirming the completeness of the reaction.

It should be noted that the final product, LaFeO$_3$, prepared by decomposition in the temperature range 600-700 °C, is a moderately agglomerated powder. After sintering the thick film in the temperature range 700-800 °C, a scanning electron micrograph reveals that the LaFeO$_3$ thick film has poor porosity, therefore the diffusion of NO$_2$ gas into the bulk takes a considerable time. The surface response is moderately quick due to the surface Fe^{3+} ions created and oxygen defects. Faster equilibrium state and gas response can be obtained after exposure to NO$_2$ gas at an operating temperature of 350 °C.

A major advantage is that the preparation of fine $LaFeO_3$ powder by thermal decomposition of the simple precursor cyano-complex is a low cost production method for the subsequent gas sensor application.

Mechanochemical processing was selected as an alternative low cost method of producing fine SnO_2 powders in a conventional ball mill.

Most of reports on mechanochemical processing that have published by other authors have discussed the use of high-energy mills. Processing of predetermined stoichiometric amounts of $SnCl_2$ with $Ca(OH)_2$ and K_2CO_3 resulted in the formation of the desired mass of SnO in a centrifugal mill. Slightly agglomerated particles were oxidised by heat treatment to SnO_2 powder with a tetragonal phase.

The main results obtained by this method may be summarized as follows:

1) The milling process itself initially results in the formation of a moderately large, slightly agglomerated SnO particles (around 1 μm) covered with a thick layer of the salt, $CaCl_2$ or KCl.

2) The chemical reaction initiated by ball milling is of great importance: when water is produced by the reaction, it will be transformed into the system as surface molecular water and hydroxide and thus subsequently considerably change the surface reactivity.

3) Synthesized powders have a very narrow particle size distribution.

4) The contamination of powder during high-energy milling has been always a major concern. One way to reduce the powder contamination is to use a high-purity inert atmosphere. It is shown that fine SnO_2 powder can be produced in the mill via centrifugal action, in air, i. e. without the requirement of an argon or a nitrogen atmosphere.

5) The SnO_2 thick film sensor's response to gas can be improved by producing powder grains smaller than 10 nm using more input energy for the milling and introduction of a grinding phase for the synthesized powder before paste preparation.

6) Preliminary gas response tests show that the SnO_2 thick film prepared from anhydrous powder has much higher response to 20 and 50 ppm of H_2S, with faster surface reaction, than that prepared from the hydrated powder. Therefore the chemical reaction, which does not produce water, is recommended for the production of powders for gas sensing applications.

7) Two interpretations of the chemical sensing mechanism are introduced. The chemical sensing mechanism of the SnO_2 thick film, prepared from anhydrous powder, should be described by the interpretation, where negatively charged surface oxygen ions react with the gas and release the electrons to the conduction band.

8) In this study Fourier transform infrared spectroscopy has been used for what we believe to be the first time in the investigation of the surface reactivity of the SnO_2 particles, produced by mechanochemical processing via centrifugal action.

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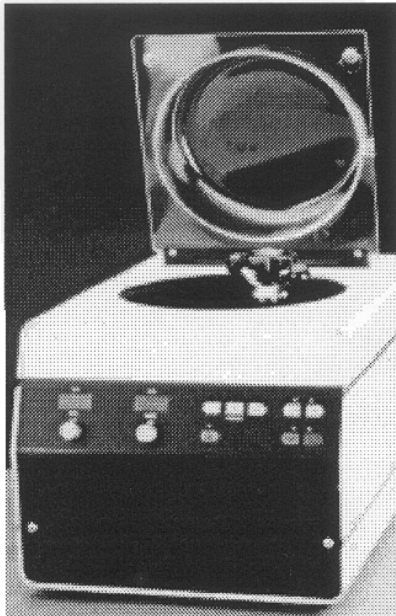
Retsch Centrifugal Ball Mill S100

S100 Centrifugal Ball Mill

Feed material	Soft, medium hard, hard, brittle
Max feed size	< 10mm
Final product	< 1 micron
Sample volume	1 x up to 250ml or 2 x up to 20ml

The Retsch S100 centrifugal ball mill is designed for fast loss-free grinding and mixing of many types of soft/medium hard/hard/brittle materials, either dry or in suspension. Simple to operate, the mill features ergonomic touch-sensitive control panel, timer, speed regulation and hinged plexiglass cover. Processing takes place within grinding jars which are available in various sizes and a choice of materials to avoid contamination due to abrasion from the grinding process (see opposite). The speed is adjustable from 0 to 650 rpm. The centrifugal forces which are generated propel the grinding balls against the inside wall of the jaw where they roll over the material to be ground. Grinding is effected primarily by impact and fraction. To counter any agglomeration effects and to enhance the homogenisation quality, the mill is fitted with an automatic reverse action system. The 100-watt brake motor will bring the unit to a complete stop in less than one second after the prescribed time elapses, or after the safety cover has been opened.
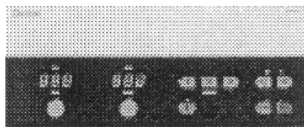
The S100 is suitable for many applications including:
Analytical Chemistry, Pharmacy, Biology, *These mills are supplied without grinding media*Mineralogy
Geology
Paints and Enamels
Nuclear Research
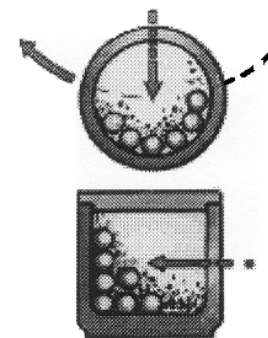
Ordering information:

09/20.189.0001	S100 for 220/240v, 50/60Hz - order grinding jars and balls separately
09/20.189.0002	S100 for 100/115v, 50/60Hz - order grinding jars and balls separately
09/22.001.0008	Universal adaptor for grinding jars type 'S', 50ml (1 for reducing/centering, 2 for stacking of non ceramic grinding jars)
09/02.112.0059	Sleeve for centering/reducing grinding jars type 'C' 50ml
09/02.362.0005	Attemperation jacket for grinding jars type 'S' 50ml
09/82.654.0001	Safe-lock fixture for hazardous materials for grinding jars type 'S' and 'C' 250ml, 125ml, 50ml
09/38.825.0001	Carry handles, one pair
	Aeration covers for type 'S' sintered alumina jars, 250ml
09/02.107.0085	Aeration cover of sintered alumina
09/02.107.0091	Aeration cover of chrome steel
09/02.107.0087	Aeration cover of stainless steel
09/02.107.0041	Aeration cover of agate
09/02.107.0086	Aeration cover of tungsten carbide
09/02.107.0131	Aeration cover of zirconia
09/01.267.0036	Spare jar holder

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