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Structure and Electric Properties of Double Magnesium Zirconium Orthophosphate

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Abstract

Double magnesium zirconium orthophosphate (MZP) is a magnesium ion conducting material. In this work, an MZP structure and properties were studied, especially in relation to its possible application as an active material in gas sensors. Double magnesium zirconium orthophosphate was produced both by sol-gel and solid state methods. The phase composition of the material was studied by X-ray diffraction method. Influence of the synthesis method on the quality of obtained material was significant. The single phase material was obtained by the sol-gel method. The precursors ($ZrOCl_2 \cdot 6H_2O$, $NH_4H_2PO_4$ and $Mg(NO_3)_2 \cdot 8H_2O$) were dissolved in water, the solutions mixed and then dehydrated for 12 h using a hot plate at 75°C. Dried powder was ball milled for 12 h and then uniaxially pressed into pellets that were sintered at various temperatures in the range of 700–1200°C. The influence of a synthesis method on electric conductivity of the samples was investigated by impedance spectroscopy (IS). Cyclic voltammetry (CV) was used to examine the possibility of application of MZP as a sensor in the presence of various gases.

Keywords: Electrical properties, Magnesium zirconium orthophosphate, Sol-gel processes, Powders - solid state reaction, Sensor material

STRUKTURA I WŁAŚCIWOŚCI ELEKTRYCZNE PODWÓJNEGO ORTOFOSFORANU MAGNEZOWO-CYRKONOWEGO

Podwójny ortofosforan magnezowo-cyrkonowy (MZP) jest materiałem przewodzącym jony magnezowe. W prezentowanej pracy badano budowę i właściwości MZP, szczególnie w odniesieniu do jego potencjalnego zastosowania w czujnikach gazowych. Podwójny ortofosforan magnezowo-cyrkonowy wytworzono zarówno metodą zol-żel, jak i metodą reakcji w fazie stałej. Skład fazowy otrzymanych materiałów zbadano za pomocą dyfrakcji promieniowania rentgenowskiego. Wpływ metody syntezy na jakość otrzymanego materiału był znaczący. Metodą zol-żel otrzymano materiał jednofazowy. Prekursory ($ZrOCl_2 \cdot 6H_2O$, $NH_4H_2PO_4$ and $Mg(NO_3)_2 \cdot 8H_2O$) rozpuszczano w wodzie, roztwory mieszano i odwadniano na płycie grzejnej o temperaturze 75°C przez 12 h. Wysuszony proszek mielono w młynie kulowym i prasowano jednoosiowo, aby uformować tabletki, które spiekano w różnych temperaturach z przedziału 700–1200°C. Wpływ metody syntezy na przewodność elektryczną próbek badano za pomocą spektroskopii impedancyjnej (IS). Woltamperometrię cykliczną (CV) w obecności różnych gazów wykorzystano do zbadania możliwości zastosowania MPZ jako czujnika gazowego.

Słowa kluczowe: właściwości elektryczne, ortofosforan magnezowo-cyrkonowy, procesy zol-żel, proszki – reakcja w fazie stałej, materiał czujnika pomiarowego

1. Introduction

Finding proper preparation methods of materials that are used in potentiometric gas sensors is essential for developing various kinds of sensors. Monitoring the concentration of pollutants in industrial fumes is very important in the current technology. The serious problem is that conductivity of most ion conductors is still too low to use them in technical applications. Moreover, sensor material must remain stable at elevated temperatures in the presence of various gases. Therefore, the choice of appropriate materials for gas sensors seems to be very important.

$MgZr_4(PO_4)_6$ (MZP) appears to be a good Mg^{2+} ion conductor. Magnesium ions have several advantages which may make the magnesium ions conductors quite attractive materials. For instance, this ion is stable in its oxidation state (+2) and has small ionic radius. Furthermore, it is not so reactive as other alkali metals and can be stable in various atmospheres. Magnesium zirconium orthophosphate as a solid electrolyte was introduced by Ikeda *et al.* [1] and successfully used to develop CO_2 potentiometric sensors [2, 3]. Wang *et al.* created SO_2 gas sensor based on MZP [4] using Na_2SO_4 as auxiliary electrode.

In this paper magnesium zirconium orthophosphate was successfully synthesized and its crystallographic and electrical properties were investigated in order to discuss its possible application as an active material in gas sensors.

2. Experimental

2.1. Samples preparation

Double magnesium zirconium orthophosphate (MZP) was produced both by sol-gel and solid state methods.

The substrates in the solid state reaction method were magnesium oxide, zirconia, and ammonium dihydrogen phosphate. They were milled either in an agate mortar or in a ball mill and calcinated in an alumina crucible for 4 h at 210°C; whole amount of powder was melted after this calcination. Then, the samples were milled again and sintered at temperature between 900°C and 1200°C.

The second method for producing $MgZr_4(PO_4)_6$ was the sol gel method. The separate water solutions of magnesium nitrate hexahydrate, zirconium oxychloride hexahydrate and ammonium dihydrogen phosphate were prepared. The magnesium nitrate and the ammonium dihydrogen solutions were mixed together to obtain transparent solution. The solution was placed onto a magnetic stirrer. The zirconium oxychloride solution and ammonia were put alternately drop by drop into magnesium nitrate and ammonium dihydrogen solution. The final solution was stirred on the hot plate for 5 h. In order to remove water from the solution it was put into a dryer for 24 h at 75°C. After drying the powder was milled and calcinated at a temperature range from 700°C to 1200°C.

The powders were used to prepare pellets. They were prepared by uniaxial pressing of powder under pressure of 700 MPa. Green bodies were sintered at a temperature range of 900-1200°C.

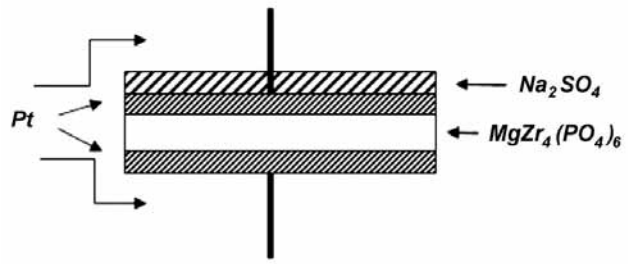

Fig. 1. Scheme of a gas senor based on MZP.

2.2. Potentiometric gas sensor preparation

Potentiometric gas sensors were produced on the base of the MZP electrolyte using Na_2SO_4 auxiliary electrode. First, platinum electrodes were brush-painted (ESL 5542 platinum paste) on the MZP pellet and platinum wires were attached. The sample with the contacts was heated at 910°C for 10 minutes. After cooling, one of the platinum electrodes was covered with Na_2SO_4 paste being an auxiliary electrode material. The MZP with auxiliary electrode was heated for 5 h at 810°C. The scheme of the sensor is presented in Fig. 1.

2.3. Measurement techniques

X-ray diffractometry was used to examine the phase composition of the prepared samples. X'Pert PRO (Philips) apparatus with CuKα radiation was used to collect diffraction spectra at room temperatures.

Impedance spectroscopy (IS) was performed on the samples with symmetric platinum electrodes to evaluate the electrical conductivity. Impedance spectra were measured in the frequency range of 1 MHz – 0.01 Hz with an excitation voltage of 50 mV by Solartron 1260 coupled with 1287 potentiostat-galvanostat. This potentiostat was also used to perform cyclic voltammetry (CV) studies and measurement of the electromotoric force (EMF). Sweep rate of 25 mV/s was applied in the voltage range of -4.5 to 4.5 V.

3. Results and discussion

3.1. X-ray diffraction measurements

All the prepared samples were investigated by X-ray diffraction method during the preparation procedure in order to choose the best synthesis conditions. Fig. 2 presents X-ray diffraction patterns of the sample prepared with the solid state method. The measured XRD pattern does not match MZP reference from the database [5]. Only one peak can be attributed to the MZP phase. It can be seen that the zirconia phosphate ($Zr_2O(PO_4)_2$) was the main present phase. Also the peaks of the secondary $(ZrO)_2P_2O_7$ phase can be seen. This result contradicts the data published by other authors [1-4] and it should be noted that within our work, the attempts of the solid state synthesis of the MZP were performed many times in a variety of conditions. Therefore, the solid state method was classified as inappropriate for the synthesis of magnesium zirconium orthophosphate.

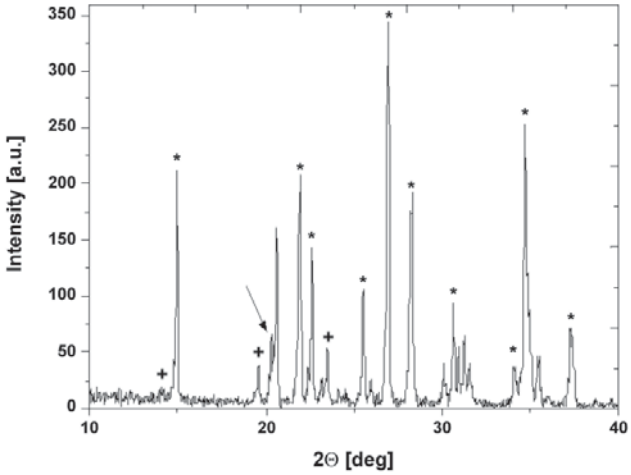

Fig. 2. X-ray diffraction pattern of sample prepared with the solid state method by sintering at 1200°C. The arrow marks the main XRD peak of the MZP phase, while (∗) and (+) correspond to the $Zr_2O(PO_4)_2$ and $Zr_3(PO_4)_4$ phase respectively.

Fig. 3 presents X-ray diffraction patterns of the samples prepared by the sol-gel method and sintered at 1000°C and 1200°C. The former sample is a single phase material. Only a trace amount of secondary phases can be seen. On the other hand, the diffractogram of sample sintered at higher temperature apart from the main MZP phase, contains noticeable peaks from other phases, *i.e.*, two zirconia phosphates.

3.2. Impedance Spectroscopy Measurements

The electrical properties of the MZP electrolyte were investigated using impedance spectroscopy. The typical impedance spectra of MZP samples are shown in Fig. 4. It is noticeable that the sample sintered at lower temperature

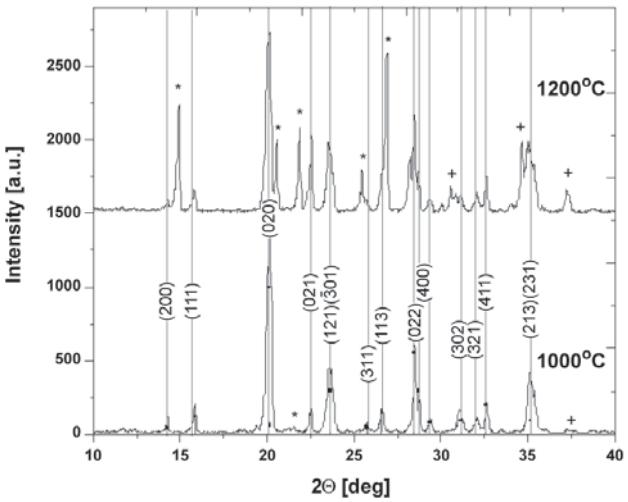

Fig. 3. X-ray diffraction patterns of MZP samples prepared by the sol-gel method followed by sintering at 1000°C and 1200°C. Peaks marked by Miller indices correspond to MZP main phase while (∗) and (+) to $Zr_2O(PO_4)_2$ and $(ZrO)_2P_2O_7$, respectively.

has lower resistivity in the whole range of temperatures. In general, the observed spectra consisted of two semicircles and an electrode contribution was observed at low frequencies. Due to the overlapping of the two semicircles, the total conductivity was calculated on the basis of the sum of grain and grain boundary resistivity.

The electric conductivities of samples sintered at various temperatures are summarized in Fig. 5.

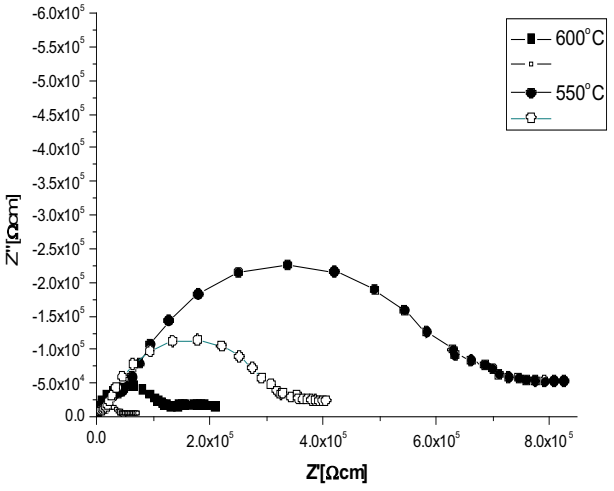

Fig. 4. Typical IS spectra measured at two temperatures for samples synthesized at 1000°C (open markers), and 1200°C (dark markers).

The conductivity measurements give an image of electrical properties of the MZP material. The conductivity level is highly influenced by the preparation route. The impedance spectroscopy measurements confirmed that temperatures higher than 1000°C are not proper for the synthesis of material with good structural and electrical properties. The samples sintered at the temperatures lower than 1150°C have two different activation energy values. This is connected with the grain or grain boundary contributions that will prevail in different temperature ranges. For the samples sintered at temperatures higher than 1000°C the activation energy seems to have only one value in the studied temperature range.

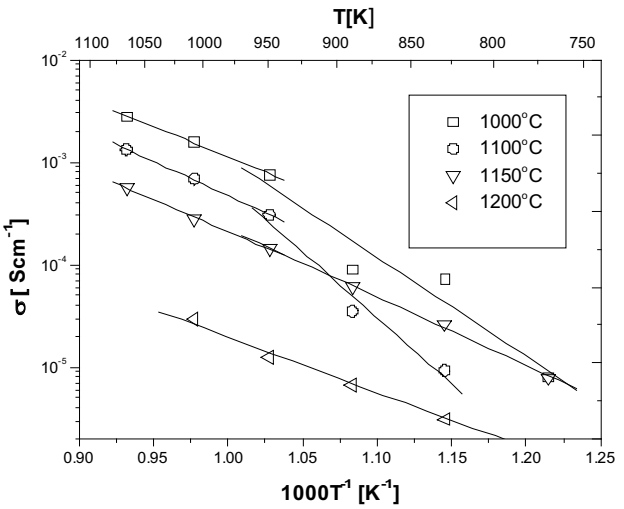

Fig. 5. Conductivity vs. temperature for MZP sintered at indicated temperatures.

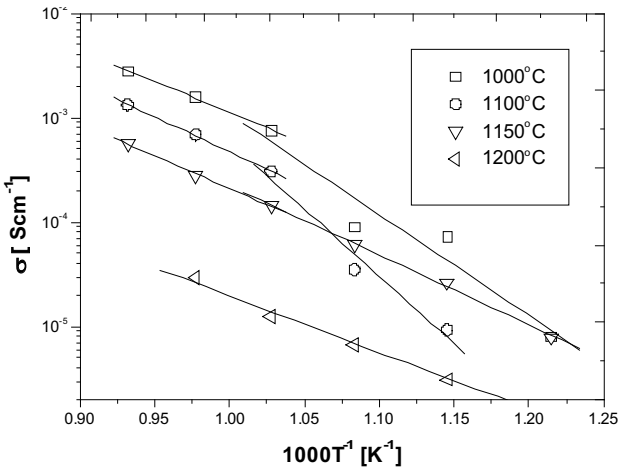

Fig. 6. CV spectrum for MZP samples in SO_2 and air atmospheres.

3.3. Cyclic voltammetry measurements

The stability of the magnesium zirconium orthophosphate in SO_2 containing atmosphere was studied with cyclic voltammetry.

The aim of these measurements was to check whether the exposure to SO_2 affects the MZP properties. Fig. 6 shows the CV characteristics for exposing MZP to SO_2 atmosphere. At the CV spectrum there is no evidence of any redox reaction occurring in the MZP material during the SO_2 exposure. The observed changes in the shape of CV curves while exposing material to gas atmosphere could be caused by the redox reaction which took place on the platinum electric contacts [4]:

$$SO_2 + \frac{1}{2}O_2 \xrightarrow{Pt} SO_3 .$$

3.4. MZP samples application in gas sensor

The sensor behaviour was investigated by measuring the relation between electromotive force of the sensor and concentration of SO_2 in the atmosphere (Fig. 7).

The electrochemical principles of operation of the MZP based sensor were investigated by Wang *et al.* [4].

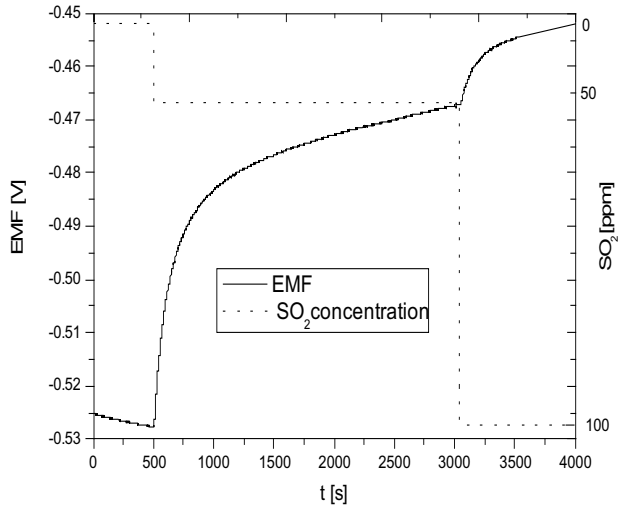

Fig. 7. MZP based sensor EMF dependency.

The sensor EMF signal in pure air was -0.525 V while during exposure to 50 and 100 ppm SO_2 it changed to -0.475 V (ΔEMF = 0.05 V) and -0.452 V (ΔEMF = 0.073 V), respectively.

The response time of the studied sensor is too long, but it cannot be interpreted as the property of the MZP material. In view of the papers on the properties of Na_2SO_4 [*e.g.*, 6], it may be caused by the choice of sodium sulphate as the auxiliary electrode. The other problem with the operation of the sensor is poor mechanical strength of the auxiliary electrode after long time of operation of the sensor. The above problems can be eliminated by using other auxiliary electrode than Na_2SO_4. Tests with barium sulphate are in progress.

4. Conclusions

Magnesium zirconium orthophosphate material was successfully synthesized, and investigated in relation to their electrical and structural properties. The proper synthesis procedure and sintering conditions were investigated in order to obtain single phase material with good level of conductivity at the sensor working temperature.

The results seem to be promising in relation to developing fully applicable gas sensor. However, the mechanical properties of both MZP and auxiliary electrode require further research.

The main goal is to find other salts that can be used to the sensor construction as the auxiliary electrode in order to measure the concentration of different pollutive gases.

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