Humidity sensor based on porous glass-ceramic

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Microstructure and phase composition of lithium titanium phosphate glass-ceramic was studied. Porous material with open porosity was obtained as a result of thermal treatment. The main crystalline phase detected was lithium titanium phosphate ($LiTi_2(PO_4)_3$). Particles of crystalline phase are very uniform in shape, with mean diameter of 2 μm and the size of pores ∼0.5 μm. It has been shown that such a glass-ceramic material can be utilised as a humidity sensor. The sensor under study works reversibly and is linear in the humidity range 6−95% RH.

1. Introduction

Humidity of air is an important parameter in the case of many electronic devices as well as domestic appliances. Many food production technologies need humidity to be controlled. People's comfort depends in great part on air humidity. Controlling humidity becomes an important task and many humidity sensors have been developed over the last decade. Most of them are based on ceramics but there are some based on polymers or organic compounds. Ceramic sensors have advantage because they can work at higher temperatures and are usually more resistant to corrosion. A good survey of modern humidity sensors was made by TRAVERSA [1]. There are two main groups of sensors: one based on resistance changes and second utilising capacitance changes. Resistance sensors are more popular because they are easy to produce and do not need sophisticated electronics to operate. They have some disadvantages also, since they usually have longer response time, can work from 10 to 95% RH, and give lower precision.

Most resistance sensors are made in the form of sintered pellet or screen-printed oxide layer. The aim of this work was to study the possibility of applying porous glass-ceramic as a humidity sensor. Glass from lithium titanium phosphate system was chosen as a base material. Porous glass-ceramic in a similar system was reported in [2]. Controlled crystallisation of such glass can lead to lithium titanium phosphate phase with NASICON type structure [3], [4]. This phase is chemically stable and has high ionic conductivity. Mobility of lithium ion can be enhanced by

water vapour adsorbed on the crystals, so such a material seems to be ideal for humidity sensor application.

2. Experimental procedure

Glass of chemical composition $SiO_2 \cdot 2.8P_2O_5 \cdot 1.2TiO_2 \cdot 2.8LiO_2 \cdot 0.2ZrO_2$ was prepared using a conventional melting method. Bath was prepared with pure reagents: Li_2CO_3, $NH_4H_2PO_4$, SiO_2, TiO_2 and ZrO_2. The synthesis was carried out in a covered alumina crucible in air. The melting temperature was 1473 K and melting time 30 min. The melting conditions are very important in the case of phosphate glasses because different melting temperature can result in a different structure of the final glass. The melt was next poured out on stainless-steel plate and samples of 3 mm in thickness were formed. Glass sample was next annealed at the temperature 10 °C above T_g temperature during 2 hours. The annealing temperature was established on DTA measurement. Samples were next crystallised to obtain glass-ceramic material. Crystallisation conditions are very important and give possibilities to control the microstructure of resulting material. In case of our glass the following crystallisation conditions were settled: temperature 550 °C, time 2 hours. After crystallisation glass was cut and polished to form $1 \times 1 \times 0.05$ cm samples. Electrodes were made with colloidal graphite paste Ted Pella Inc. Samples were connected to the measuring system through platinum electrodes tightened to graphite electrodes by means of a spring. The measuring system is shown schematically in Fig. 1.
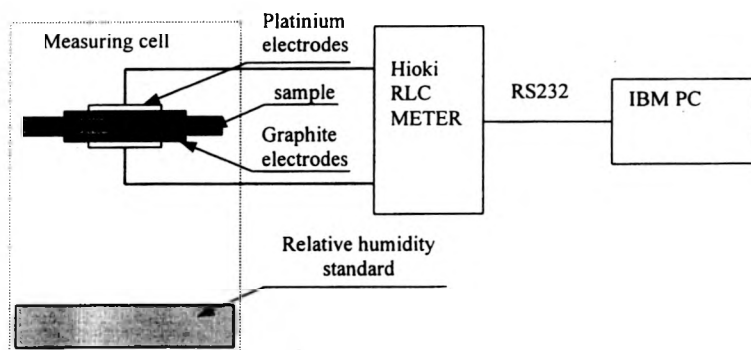

Fig. 1. Schematic of the measuring system.

T a b l e. Relative humidity standards.

Compound	Temperature range [°C]	Relative humidity at 25 °C [%]
$KOH \cdot 2H_2O$	5 − 30	9
$MgCl_2 \cdot 6H_2O$	5 − 45	33
$Mg(NO_3)_2 \cdot 6H_2O$	5 − 35	53
NaCl	10 − 40	75
KNO_3	0 − 50	92

Humidity inside the measuring cell was established using RH standards [5], [6]. Standards utilised in this work are also listed in the Table.

The DTA measurement was made on Q1500 derivatograph with 10 °C/min. Crystalline phases were identified with an X-ray diffractometer type SEIFERT XRD7 using Cu K_α radiation. Electric analysis was curried out on Hioki 3532 RLC meter supported by a computer. Morphology of the samples was observed by scanning electron microscope JOEL 5400 with Link X-ray microprobe facility.

3. Results and discussion

3.1 Thermal analysis, porosity and density

The result of thermal analysis of the glass is shown in Fig. 2. Transformation temperature T_g is relatively low (445 °C). Crystallisation occurs at 550 °C. The peak is strong and sharp, which indicates rapis volume crystallisation. Porosity measured
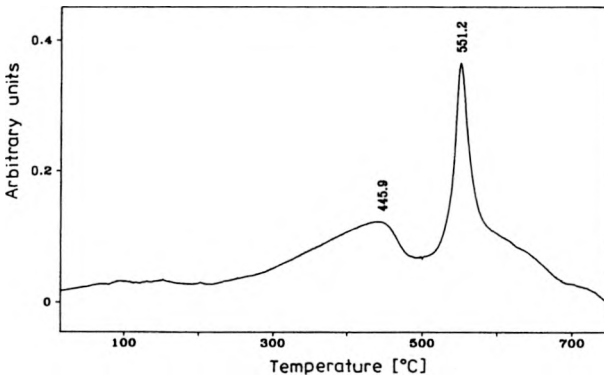

Fig. 2. Result of thermal analysis of the glass.

by BET method was 0.1 m/g in the case of glass and 0.5 m/g for devitrificate. It means that the pores observed by SEM are too large to be measured by BET. The density of glass is 2.55 g/cm³ and decreases to 2.45 g/cm³ after crystallisation.

3.2. X-ray results

Thermal treatment at 550 °C leads to crystallisation of three phases: titanium phosphate, lithium titanium phosphate and tridymite. The predominant phase was lithium titanium phosphate ($\sim 90\%$), but the first phase to occur during crystallisation was titanium phosphate, acting as nucleator of lithium titanium phosphate phase crystallisation (Fig. 3a,b).

3.3. SEM microstructure observation

The early stage of crystallisation, morphology of crystalline phase and microstructure of glass-ceramic were studied by electron microscope, as shown in Fig. 4. The first picture (a) was taken for glass crystallised at the nucleation temperature of
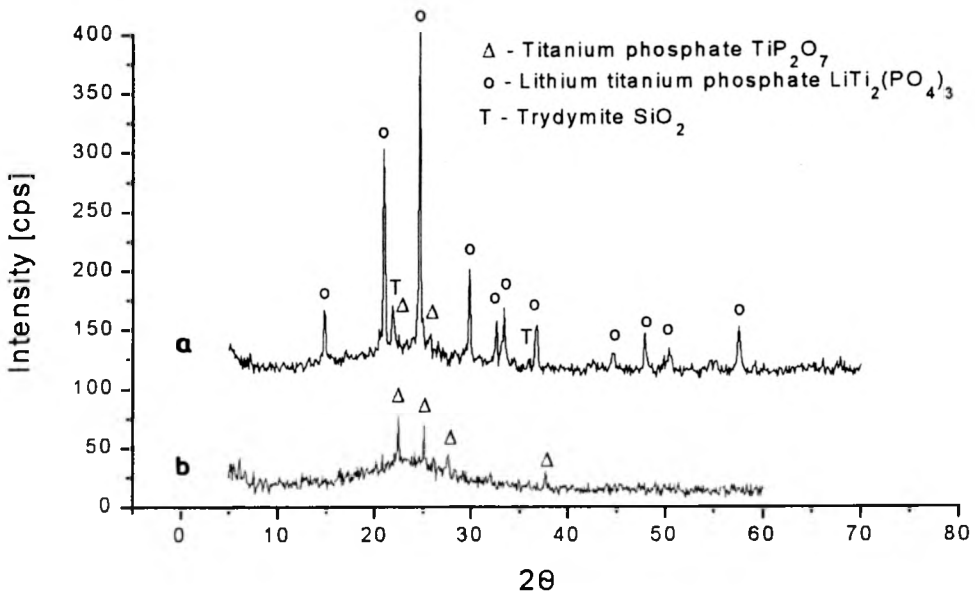
Fig. 3. X-ray diffraction pattern: **a** — early stage of crystallisation, **b** — glass-ceramic.
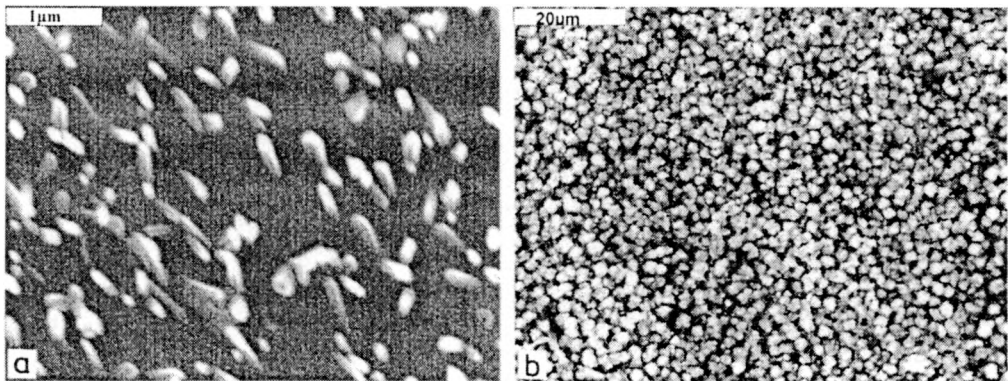

Fig. 4. SEM observation of microstructure: **a** — titanium phosphate crystals at an early stage of crystallisation, **b** — glass-ceramic microstructure.

500 °C. Small crystals (~ 0.5 μm) of titanium phosphate are clearly seen. These crystals act as crystallisation centres and promote volume crystallisation. Full crystallisation leads to the microstructure shown in Fig. 4b. Crystals are round in shape with a very uniform size about 4 μm. There are many pores of $1-3$ μm in diameter. Material with such a microstructure and open porosity is very promising for humidity sensor applications. The surface area is relatively large and the pores are large enough to avoid capillary condensation. High ionic conductivity of the main crystalline phase [7], [8] is advantageous in the case of low humidity measurements <20% RH.

3.4. Impedance spectroscopy

The relation between RH and impedance spectroscopy is shown as a Nyquist plot in Fig. 5. There is one relaxation time observed, so equivalent circuit for such a system is in the form of parallel-connected ideal capacitance and resistance. The impedance
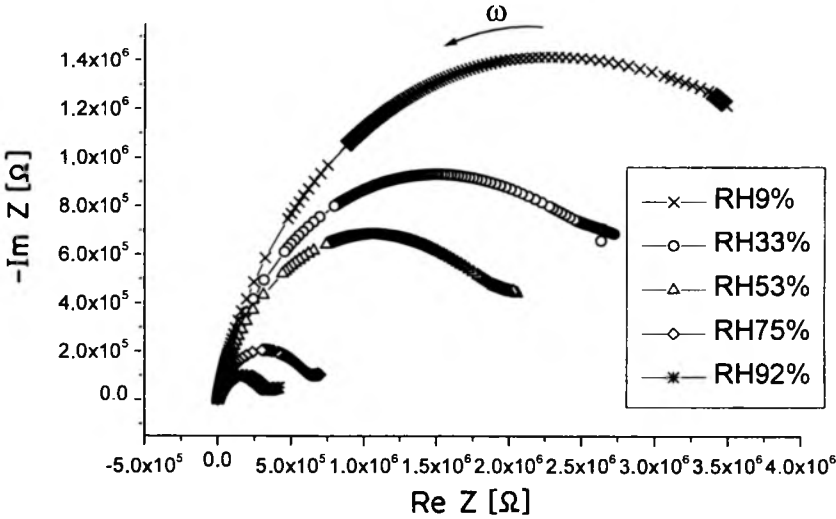
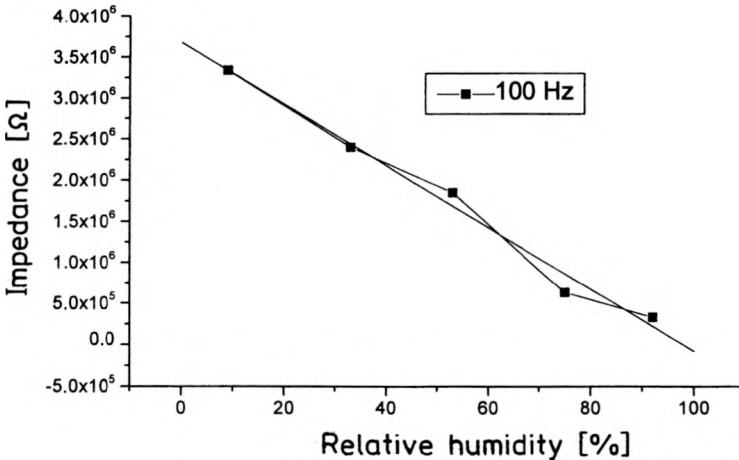Fig. 5. Nyquist graph of humidity sensor for different relative humidities.

Fig. 6. Impedance as a function of relative humidity measured at 100 Hz.

as a function of humidity for one selected frequency of 100 Hz is linear in the measuring range of 6−95% RH (Fig. 6). There is no chemical reaction with water vapour, so the sensor works in a reversible manner. The response time is about 5 min and is rather long, mainly because of big thickness of the sample.

4. Conclusions

Porous glass-ceramic based on lithium titanium phosphate is a promising material for humidity sensors. The main crystalline phase ($LiTi_2(PO_4)_3$) is chemically stable and exhibits high ionic conductivity, which gives the possibility of applying such a sensor at a very low humidity. There is no water vapour condensation. The sensor works reversibly and electric response is linear in the range $6-95\%$ RH.

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