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STUDY OF NOVEL OXIDE MATERIALS FOR FUEL CELLS APPLICATION

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ABSTRACT
The dense glass-crystalline and amorphous samples from ternary Ti-V-P oxides have been prepared through a solid-state reaction using melt quenching method. The samples have been studied with respect to their structure and electrical behaviours with a view of fuel cell application. They are structured from phosphorous net with inclusions of TiO2 and V2O5 structure units. The increase of TiO2 amount simplifies the depolimerization of the net while the V2O5 units are integrated in the matrix. Two main structures NASICON and Rutile type have been defined in the glass-crystalline samples. The electrical conductivity measurements show an enhanced conductivity at higher temperature and lower TiO2 content. First results suggest the materials are advantageous to come into use in fuel cells.

INTRODUCTION
Fuel cells have attracted worldwide attention as a clean power source because of the high efficiency in energy conversion and low emissions. Fuel cell technologies continue to advance rapidly and new technical milestones are achieved, and a range of fuel cell technologies in material handling, transportation and stationary power applications moved toward commercialization.

Key element in the fuel cell assembly is the electrolyte. The role of the materials science is essential for discovering and developing electrolyte materials that support high ion conductivities (and negligible electronic conductivities), together with good chemical stability and simply fabrication (Malavasi L at.al, 2010).

One major shortage of the solid oxide fuel cells (SOFCs) is the high operation temperature region 800 – 1000°C . The decrease of the working temperature is an important challenge in the fuel cells science and technology. One of the crucial issues in lowering the working temperature to the range 300 – 500°C is to explore new electrolyte materials. The development of novel materials is priority in terms of long-term safety operation and devices stability (Haile S. 2003).

The oxide glasses are very prospective materials for intermediate temperature fuel cells (IT-SOFC) application as they are stable and proton conductive in this temperature region. Protons in oxide glasses usually remain as X - OH groups (X = Si, P, etc.) in a glass structure when glasses are prepared via a melting process at ambient atmosphere (Uma T. and Nogami M. 2006). Arai at all. (Arai, at all . 1986) reported about a significant contribution of residual P - OH groups in phosphate glasses on the electrical conduction.

NASICON based phosphates are among the materials widely studied in the past decades (Vijayan L. and Govindaraj G. 2012). Materials like LiTi2(PO4)3, Na3Cr2(PO4)3 and Li3Fe2(PO4)3 are interesting system because of their high ion conductivity at room temperature.
Our work is focused on new TiO$_2$-V$_2$O$_5$-P$_2$O$_5$ glass and glass-crystalline materials prepared by means of melt quenching method and on the effect of TiO$_2$ on the structural and electrical behaviours.

EXPERIMENTAL

Melt quenching method reported elsewhere was applied for the preparation of bulk materials from the ternary oxide TiO$_2$-V$_2$O$_5$-P$_2$O$_5$ system. The initial powdered TiO$_2$ and V$_2$O$_5$ and orthophosphoric acid H$_3$PO$_4$ were mixed, heated stepwise in air atmosphere for several hours in a furnace and quenched. After rapid cooling samples with compositions (TiO$_2$)$_x$(V$_2$O$_5$)$_y$(P$_2$O$_5$)$_{100-x-y}$, where x = 5, 10, 15, 20 mol % and y = 30, 40, 50, 60, 70 mol.% were obtained.

Structure analyses were performed by XRD and IR spectroscopy methods. Data from X-ray diffractometer model Philips APD-15 were collected in angle region 20 = 20°÷60°, with a constant step of 0.02 deg.s⁻¹ at wavelength λ = 1.54178 Å of CuKα tube at ambient temperature. IR spectrophotometer EQUINOX 55 (Brucker instrument) in the spectral region from 4000 to 400 cm$^{-1}$ was used for the comprehensive structure study. The conductivity measurements were carried out on the polished samples with particular dimension of 1 cm$^2$ with silver pasted contacts. Autolab PGSTAT 30 (Eco Chemie) frequency response analyzer, in the frequency range 0.05Hz - 1MHz was used to perform impedance measurements. The study was accomplished in the temperature range from 20 to 120°C with a step of 20°C.

RESULTS

XRD

The XRD analysis determined two of the samples as amorphous (Table 1, samples 1 and 2) and two other – as glass-crystalline (amorphous with nanocrystalline inclusions). Peaks detected on the XRD spectrum of sample 3 belong to rutile phase incorporated in the amorphous matrix. Crystal structure of sample 4 corresponds to the NASICON type, mixed metal-phosphate structure $\text{A}_x\text{B}_2(\text{PO}_4)_3$, where A is an one-valence ion and B is a variable-valence ion (fig.1.).

<table>
<thead>
<tr>
<th>№</th>
<th>Composition</th>
<th>State</th>
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<tbody>
<tr>
<td>1</td>
<td>(TiO$_2$)$_5$(V$_2$O$<em>5$)$</em>{70}$ (P$_2$O$<em>5$)$</em>{25}$</td>
<td>amorphous</td>
</tr>
<tr>
<td>2</td>
<td>(TiO$<em>2$)$</em>{10}$(V$_2$O$<em>5$)$</em>{50}$(P$_2$O$<em>5$)$</em>{40}$</td>
<td>amorphous</td>
</tr>
<tr>
<td>3</td>
<td>(TiO$<em>2$)$</em>{20}$(V$_2$O$<em>5$)$</em>{30}$(P$_2$O$<em>5$)$</em>{30}$</td>
<td>glass-crystalline (rutile)</td>
</tr>
<tr>
<td>4</td>
<td>(TiO$<em>2$)$</em>{10}$(V$_2$O$<em>5$)$</em>{30}$(P$_2$O$<em>5$)$</em>{30}$</td>
<td>glass-crystalline (NASICON)</td>
</tr>
</tbody>
</table>
Structure study

FT-IR is one of the most general spectroscopic techniques used to identify the functional groups in materials. It is an important and popular tool for structural exposition and compound identification. The spectra of the amorphous samples differs from the spectra of glass-crystalline by shape and peaks as visualized in fig. 2.

The structure of the glass-crystalline materials under study is composed from Q^2 tetrahedra forming network with asymmetric stretching vibration of P=O bond at ~1270 cm⁻¹, polymeric metaphosphoric chains from Q^2 tetrahedra with (PO₂) bond asymmetric vibration at ~1280 cm⁻¹ and symmetric stretching vibration at 1100 cm⁻¹. "Inverted" glasses, are based on either/both: pyro (Q¹) with a structural unit of (PO₃)₂ group which stretching vibration is found at ~1050 cm⁻¹ and orthophosphatic (Q⁰) with main structural group of (PO₄)³⁻ tetrahedra with stretching mode located at 1000 cm⁻¹.

The absorption band at 1020 cm⁻¹ of the glass-crystalline samples is much more broader and composed of two overlapping peaks. The FTIR spectra of NASICON materials are dominated by intense, overlapping intramolecular PO₄⁻ stretching modes (ν₁ and ν₃) that range from 1300 to 700cm⁻¹.

The absorption band at 1020 cm⁻¹ is due to VO₅ groups which are part of deformed octahedra. The mode around 838-820 cm⁻¹ is assigned to V-O-V bending. The VO₅ groups constituite deformed trigonal bipyramids with one vanadium ion in the center of the polyhedron and one shorter V=O (vanadyl) bond. Addition of modifier (phosphor) introduces non-bridged oxygen atoms in the glass and leads to depolymerization of the phosphate network by oxygen atoms that destroy P-O-P bridge structure. This absorption band indicates that the phosphate network is built from short chains and pyrophosphate groups (P₂O₇⁴⁻) after the polymerization destroy. The 811cm⁻¹ mode might be due to the mixed V-O-Ti bonds.

With increase in titanium content in the samples up to 10 mol %, patterns of FTIR spectra remain the same except the bands around 1210 and 1280 cm⁻¹. The structure of titanium oxides consist of TiO₆ octahedra. These octaedra in the rutile structure are connected to six other octahedra by the apexes while in the NASICON structure the TiO₆ octahedra are connected to six PO₄ tetrahedra.
Electrical conductivity

Figure 3 represents the complex-plane impedance (Nyquist) plots of the samples with NASICON and Rutile structures (sample 3 and 4). Two semicircles (arc) are observed for the both samples and they can be interpreted from structure point of view. The two phases observed on the diffractograms: crystalline and amorphous correspond to the two arcs on the impedance plots. They define crystalline grains and the area between them (grain boundary) where the glassy phase is distributed. The simplest equivalent circuit describing two phase model consists of two Voigt (R and Capacitor or Constant Phase Element in parallel - R/CPE) elements in series (Stoynov Z. and Vladikova D. 2005)

The high-frequency semicircle is due to ac response of the grains Rgr/CPEgr while the lower-frequency part expresses electrical properties of glass matrix Rgl/CPEgl. The conductivity is obtained using fitting procedure and the activation energies are determined from slopes of the Arrhenius plots (lnσ versus 1/T) presented in fig.4. The first arc of the (TiO2)20(V2O5)30(P2O5)30 sample is connected with ac response of the Rutile phase, however the obtained conductivity is (σgr-rutile= 9.9x10^-8 S.cm^-1) much higher compared with the pure TiO2-Rutile (σrutile≤10^-12 S.cm^-1). It is well known that the electrical conductivity of undoped Rutile is very dependent on sample preparation conditions like temperature, atmosphere during sintering and cooling rate. The samples become increasingly semiconducting when quenched from temperatures above ~700°C in ambient atmosphere (Liu Y and West A. 2013). On the other side the solid solution of Rutile with vanadium exhibits also semiconducting properties (Tena M. et.al 2004)
The increase of the V$_2$O$_5$ content leads to an increase in the conductivity in two orders in respect to sample with rutile structure. The results propose that vanadium is incorporated into NASICON type crystal structure.

Fig. 4 shows the Arrhenius plots of the conductivity of the glass-crystalline samples determined from the complex impedance method. The logarithm of the conductivity changed linearly versus $1/T$ over a wide range of temperatures from 20 to 220 $^\circ$C. The conductivity increased and the activation energy decreased with the temperature and the decrease of the TiO$_2$ content.
DISCUSSION

It is accepted that proton transport is dependent on the interface region in the composite materials. The presence of hydrogen bonds and grain boundaries in the oxides is advantageous for the proton conduction process. Based on these arguments and on the results from this study we may propose that the material under this study can act as electrolyte in a fuel cell working in the intermediate-temperature region. The glass-crystalline samples are more beneficial compared to amorphous samples showing better conductivity values. The small TiO$_2$ content introduces additionally interface and supplies high conductive paths. The presence of titanium facilitates the depolymerization of the phosphate network and appearance of isolated orthophosphate structural units.

One of the best strategies for achieving high proton conductivities is to synthesise cation-offstoichiometric materials. The charge imbalance caused by the cation non-stoichiometry is compensated by protons. Phosphates are among the materials with high-temperature proton conduction receiving much attention. Depolymerization of the phosphate network and incorporation of vanadium ions produces new pathways by modification and deformation of the crystal structure. Further studies in the hydrogen and oxygen atmosphere already performed approve the good chances of these materials to be used in midtemperature fuel cells.

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REFERENCES


