Bulgarian Chemical Communications, Volume 45, Special issue A (159 – 162) 2013

Investigations of glass-crystalline TiO_2-V_2O_5-P_2O_5 samples

D. V. Blaskova-Kochnitcharova[1, 2], T. Petkova[2]*, L. Fachikov[1], E. Lefterova[2], I. Kanazirski[3], P. Angelov[2], S. Vassilev[2]

[1]*University of Chemical Technology and Metallurgy, 8, Kl. Ohridski Blvd., 1756 Sofia, Bulgaria*
[2]*Institute of Electrochemistry and Energy Systems, Bulgarian Academy of Sciences, Acad. G. Bontchev Str., Bl. 10, 1113 Sofia, Bulgaria*
[3]*University of Mining and Geology "St. Ivan Rilski", 1756 Sofia, Bulgaria*

Received March 19, 2013; revised April 23, 2013

Bulk samples of the ternary system TiO_2-V_2O_5-P_2O_5 have been synthesized by standard melt quenching technique. The structure of the materials has been studied by X-ray diffraction. The obtained samples possess glassy-crystalline structure. Impedance investigations have been performed by using impedance spectroscopy at different temperatures. The spectra are analyzed by two phase concept: crystalline grains distributed in glassy matrix The conductivity is obtained using fitting procedure. The conductivity is most likely caused by polaron hopping between aliovalent vanadium ions.

Keywords: oxides, X-ray diffraction, impedance analysis

INTRODUCTION

The oxide semiconductors are large group of the semiconducting glassy alloys. The electrical properties of oxide glasses containing transition-metal ions such as V, Fe and W are of interest because of their switching properties. The semiconducting behaviors of the glasses are due to the presence of transition-metal ions in more than one valence state. Oxide glasses with high content of V_2O_5 exhibit considerable electronic conductivity governed by cross-linking of the glass network supporting enhanced electron hopping along V^{4+}- O- V^{5+} bonds [1-2].

Pietrzak *et al.* [3] have shown that vanadate–phosphate glasses with a composition $90V_2O_5$-$10P_2O_5$ undergo thermal nanocrystallization, which leads to a significant increase in the electronic conductivity.

Hirashima *et al.* [4] have studied TiO_2-V_2O_5-P_2O_5 glasses containing up to 30 mol% TiO_2 at different temperatures and have established that the ternary glasses are semiconducting due to polaron hopping similarly to the V_2O_5-P_2O_5glasses. The d.c. conductivity has been established to decrease when V_2O_5 is replaced by TiO_2 but increases when P_2O_5 is replaced by TiO_2. The variations of the conductivity values are mainly due to changes in the activation energy.

The aim of the present work is to study electrical transport in the ternary TiO_2-V_2O_5-P_2O_5 glass-crystalline materials with a view to their further application in electrochemical systems.

EXPERIMENTAL

Bulk samples with compositions $(TiO_2)_{20}(V_2O_5)_{50}(P_2O_5)_{30}$ and $(TiO_2)_{10}(V_2O_5)_{60}(P_2O_5)_{30}$ were synthesized by melt-quenching method. As row materials were used powders of TiO_2 and V_2O_5 and liquid H_3PO_4. The samples were thoroughly ground (homogenized) in agate mortar, melted in quartz crucibles at temperature 1000-1200 °C and fast cooled between ice cold copper plates. To obtain samples with a specific form required for impedance measurements, the melts were cooled in a copper matrix with 1 cm diameter, depth of 1 mm and pressed with copper plate.

The phase formation of the samples was studied by X- ray diffraction (XRD) method. XRD patterns were recorded by means of X-ray diffractometer Philips APD-15. The data were collected with a constant rate of 0.02 deg.s^{-1} over an angle range $2\theta = 20°\div70$ deg using CuK_α radiation ($\lambda = 1.54178$ Å). All X-ray investigations were performed at ambient temperature.

The preparation of the samples for impedance study included polishing and deposition of silver paste contacts on the surfaces. The impedance measurements were carried out by means of

* To whom all correspondence should be sent:
E-mail: tpetkova@bas.bg

Autolab PGSTAT 30 (Eco Chemie) frequency response analyzer, in the frequency range 0.05Hz - 1MHz. The study was performed at different temperatures in the temperature range from 20 to 120°C with a step of 20°C.

RESULTS AND DISCUSSION

- *XRD*

XRD spectra of the synthesized samples are presented in Fig. 1. The spectra show a combination of broad diffraction halos and crystalline peaks, which prove the glassy-crystalline structure. Peaks of rutile (TiO_2) (JCPDS-PDF#89-4202) are obtained on the XRD-spectrum of the $(TiO_2)_{20}(V_2O_5)_{50}(P_2O_5)_{30}$ sample. The peak positions on the $(TiO_2)_{10}(V_2O_5)_{60}(P_2O_5)_{30}$ diffractogram are very close to those of the compounds $Ti_4P_6O_{23}$ (JCPDS-PDF#39-0004), $NaTi_2(PO_4)_3$ and $NaVTi(PO_4)_3$ (JCPDS-PDF #49-1114, #84-2012). The crystalline structure of the last two corresponds to NASICON type structure (acronym of Na Super Ionic Conductor). This is mixed metal phosphates type structure with a general formula $A_xB_2(PO_4)_3$, where A is a monovalent ion and B is ion in three, tetra, or penta-valent state [5, 6]. The structure is described as a covalent skeleton $[B_2(PO_4)_3]^-$ consisting of the PO_4 tetrahedral and the BO_6 octahedral units, forming 3D interconnected channels with two types of interstitial spaces M_I and M_{II}, where conducting A^+ cations are distributed. When cations are absent (x=0) the NASICON structure is termed empty. Since this structure is discovered in some binary and ternary metal phosphates like $NbTi(PO_4)_3$, $NbV_{0.5}Ti_{0.5}(PO_4)_3$ [6] our hypothesis is that titan-vanadium phosphate possesses empty NASICON structure. It is correlated with the investigation of S. Titlbach and co-workers, who has established the NASICON related structure in vanadyl (V) titanium(IV) phosphate with structural formula $(V^VO)Ti^{IV}_6(PO_4)_9$ [7].

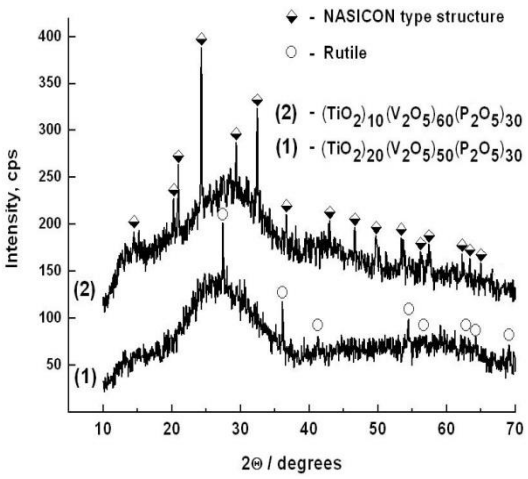

Fig. 1. X-ray diffraction patterns of $(TiO_2)_{20}(V_2O_5)_{50}(P_2O_5)_{30}$ and $(TiO_2)_{10}(V_2O_5)_{60}(P_2O_5)_{30}$ samples.

- *Impedance*

Figure 2 represents the complex-plane impedance (Nyquist) plots of the samples under investigation. Two semicircles (arc) observed for the both samples are interpreted with two phase concept. The phases observed on the diffracto-grams: 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 elements in series, as presented in Fig. 2c. (Voigt element is R and Capacitor - R/C or R and Constant Phase Element-R/CPE in parallel) [8, 9]. The high-frequency semicircle is due to ac response of the grains R_{gr}/CPE_{gr} while the lower-frequency part expresses electrical properties of glass matrix R_{gl}/CPE_{gl}. The conductivity is obtained using fitting procedure and the activation energies are determined from slopes of the Arrhenius plots ($\ln\sigma$ versus 1/T) presented in fig.3. The calculated values of the conductivity at room temperature and activation energy are presented in Table 1.

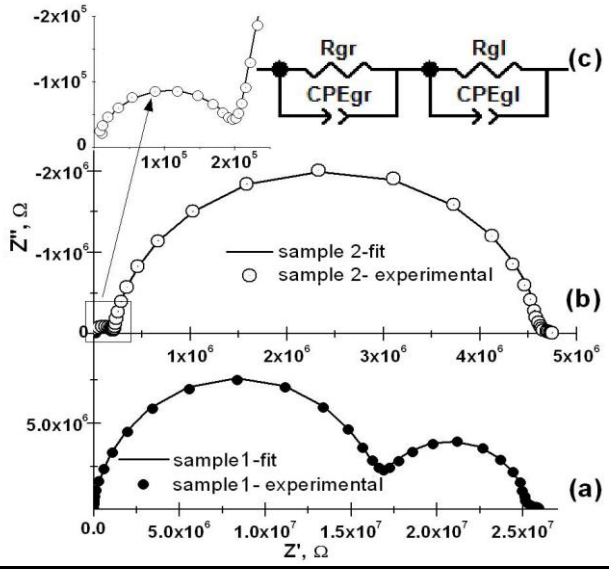

Fig. 2. Nyquist plots of (a) $(TiO_2)_{20}(V_2O_5)_{50}(P_2O_5)_{30}$; (b) $(TiO_2)_{10}(V_2O_5)_{60}(P_2O_5)_{30}$ samples and (c) equivalent circuit.

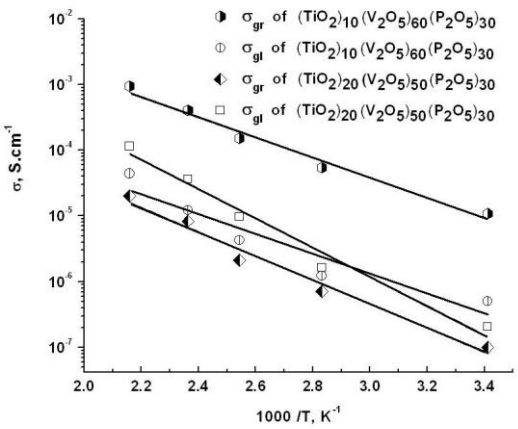

Fig. 3 Arrhenius plots of the conductivities of $(TiO_2)_{20}(V_2O_5)_{50}(P_2O_5)_{30}$ and $(TiO_2)_{10}(V_2O_5)_{60}(P_2O_5)_{30}$ glass-crystalline samples.

The first arc of the $(TiO_2)_{20}(V_2O_5)_{50}(P_2O_5)_{30}$ sample is connected with ac response of the rutile phase, however the obtained conductivity is ($\sigma_{gr\text{-}rutile}$= $9.9x10^{-8}$ $S.cm^{-1}$) much higher compared with the pure TiO_2-rutile ($\sigma_{rutile}\leq10^{-12}$ $S.cm^{-1}$). 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 [10]. On the other side the solid solution of rutile with vanadium exhibits also semiconducting properties [11]. The values of conductivity ($\sigma_{gr\text{-}rutile}$) and activation energy of the samples under this study are close to those of the $Ti_{0.91}V_{0.09}O_2$

Table 1. Conductivities and activation energies of the $(TiO_2)_{20}(V_2O_5)_{50}(P_2O_5)_{30}$ and $(TiO_2)_{10}(V_2O_5)_{60}(P_2O_5)_{30}$ glass -crystalline samples.

Sample	σ_{gr} $S.cm^{-1}$	E_{agr} eV	σ_{gl} $S.cm^{-1}$	E_{agl} eV
$(TiO_2)_{20}(V_2O_5)_{50}(P_2O_5)_{30}$	$9.9x10^{-8}$	0.37	$2.1x10^{-7}$	0.44
$(TiO_2)_{10}(V_2O_5)_{60}(P_2O_5)_{30}$	$1.1x10^{-5}$	0.31	$5.0x10^{-7}$	0.30

and this suggests that higher conductivity of the samples with higher TiO_2 content is due most probably to inclusion of vanadium into the rutile structure.

The increase of the V_2O_5 content (sample $(TiO_2)_{10}(V_2O_5)_{60}(P_2O_5)_{30}$) leads to an increase in the $\sigma_{gr\text{-}nasicon}$ conductivity in two orders in respect to $\sigma_{gr\text{-}rutile}$. The conductivity values of the glassy components caused by electron hopping between V^{4+} and V^{5+} centers (polaron conductivity) are very alike in the both samples. The results propose that vanadium is incorporated into NASICON type crystal structure which correlates with XRD results.

CONCLUSIONS

The conclusions drawn from the results obtained in this study can be summarized as follows:

- the investigated oxide system reveal two phase glassy-crystalline structure;
- the XRD results demonstrate that the crystalline phase in the sample with lower titanium content is mixed titan-vanadium phosphate with NASICON type crystal structure while the diffraction peaks in the sample with higher titanium concentration belong to rutile phase;
- The conductivity of the glass crystalline samples is most likely caused by polaron hopping between polyvalent vanadium ions.

Acknowledgments: *D. Blaskova-Kochnitcharova acknowledges the financial support of project BG 051PO001-3.3.06-0038.*

REFERENCES

1. P. Jozwiak, J. E. Garbarczyk, M. Wasiucionek, *Mater. Sci. -Poland*, **24**, 147 (2006).
2. M-C. Ungureanum, M. Levym, J-L Souquet, *Ceram. Silik.*,**44,** 81 (2000).
3. T. K. Pietrzak, J. E. Garbarczyk, M. Wasiucionek, I. Gorzkowska , J. L. Nowinski, S. Gierlotka, *Solid State Ionics*, **192**, 210 (2011).
4. H. Hirashima, K. Nishi, T. Yoshida, *J. Am. Ceram. Soc.*, **66**, 704 (1983).
5. S. Benmokhtar, A. El Jazouli, A. Aatiq, J.P. Chaminade, P. Gravereau, A. Wattiaux, L. Fournes, J.C. Grenier, *J. Solid State Chem.*, **180**, 2004 (2007).
6. P.A. Agaskar, R.K.Grasselli, D.J.Butterey and B. White, in Third World Congress on Oxidation Catalysis, by S.T. Oyama, A.M. Gaffney, J.E. Lyons, R.K. Grasselli (eds), Elsevier Science B.V, 1997, p. 219.
7. S. Titlbach, W. Hoffbauer, R. Glaum, *J. Solid State Chem.*, **196**, 565 (2012).
8. Z .Stoynov, D.Vladikova, Differential Impedance Analysis, Marin Drinov Publishing House, 2005.
9. N. Bonanos, B.C.H. Steele, E.P. Bulter, Application of Impedance Spectroscopy, in Impedance Spectroscopy, Theory, Experiment, and Applications, E. Barsoukov, J. Ross Macdonalds (eds), John Wiley & Sons, Inc., Hoboken, New Jersey, 2005, p. 205.
10. Y. Liu, A.R. West, *J. Am. Ceram. Soc*., **96,** 218 (2013).
11. M.A. Tena, M. Llusar, J.A. Badenes, J. Calbo, G. Mondros, *J. Mater. Sci.& Mater. Electronics*, **15**, 265, (2004).

ИЗСЛЕДВАНЕ НА TiO_2-V_2O_5-P_2O_5 СТЪКЛО-КРИСТАЛНИ МАТЕРИАЛИ

Д. В. Блъскова-Кошничарова[1,2], Т. Петкова[2*], Л. Фачиков[1], Е. Лефтерова[2], И. Каназирски[3], П. Ангелов[2], С. Василев[2]

[1]Химикотехнологичен и Металургичен Университет, бул."Кл. Охридски" 8, 1756, София, България
[2]Институт по Електрохимия и Енергийни системи, Българска Академия на Науките, ул. „Акад. Г. Бончев" бл.10, 1113, София, България
[3]Минно-Геоложки Университет ул."Св. Иван Рилски", София, 1700 България

Постъпила на 19 март 2013 г.; Преработена на 23 април 2013 г.

(Резюме)

Синтезирани са образци от системата TiO_2-V_2O_5-P_2O_5 по метода на бързото охлаждане. Структурата на материалите е изследвана с рентгенова дифракция. Установено е, че образците имат стъкло-кристална структура. Имеданските изследвания са проведени при различни температури. За определяне на проводимостта, получените спектри са анализирани и апроксимирани с двуфазен модел (кристални частици, разпределени в стъклообразна матрица). Проводимостта се обяснява с поларонни прескачания между алиовалентните ванадиеви йони.