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Network modification of phosphate materials by transition metals doping

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This work is focused on structural modification of phosphate materials by doping with transition metal oxides. The structure of $(TiO_2)_x(V_2O_5)_y(P_2O_5)_{100-x-y}$ composites is discussed in terms of composition, structural units and valence variations. XRD diffraction, IR and XPS spectroscopic techniques are used to analyze the materials. The addition of V_2O_5 and TiO_2 destroys P-O-P bridge structure, generates mixed P-O-V bonds and non-bridged oxygen atoms leading to the appearance of isolated PO_4^{3-} units.

Keywords: transition metal oxide, structural study, IR, XPS

INTRODUCTION

The need of urgent development of alternative energy sources continuously increases. The solid oxide fuel cells (SOFCs) are a promising response since they can operate reversibly, storing excess of renewable electricity in electrolysis mode, and then converting the fuel back to electricity in fuel cell mode [1]. The most favourable approach in SOFCs optimization is to lower the operating temperatures (200-600 ºC). Composite materials with charge imbalance caused by the cation non-stoichiometry compensated by protons (cation off-stoichiometric materials) are among the promising candidates for SOFC electrolytes. The non-stoichiometry is a typical behaviour of the transition metals that can influence the materials properties. With incorporation of transition metal ions, one may introduce non-stoichiometry and create new pathways for proton mobility due to structure reformation [2, 3]. In this respect, the phosphate materials like phosphate glasses, metal pyrophosphates and metal phosphates with NASICON type structure are an interesting subject of scientific work [4-6].

The present study discusses structural modification of $(TiO_2)_x(V_2O_5)_y(P_2O_5)_{100-x-y}$, composites with x = 10, 20 mol % and y = 45, 50, 60 mol % after doping with transition metal.

EXPERIMENTAL

Bulk samples from $(TiO_2)_x(V_2O_5)_y(P_2O_5)_{100-x-y}$ system were synthesized by melt quenching method. The initial compounds of TiO_2 and V_2O_5 powders and orthophosphoric acid (H_3PO_4) were homogenized and melted at 1100 ºC to obtain samples with compositions:

$(TiO_2)_{10}(V_2O_5)_{45}(P_2O_5)_{45}$ (N1),
$(TiO_2)_{10}(V_2O_5)_{50}(P_2O_5)_{40}$ (N2),
$(TiO_2)_{10}(V_2O_5)_{60}(P_2O_5)_{30}$ (N3),
$(TiO_2)_{20}(V_2O_5)_{50}(P_2O_5)_{30}$ (N4).

The structure of the samples was studied by X-ray diffractometer Philips APD-15 using CuK_α radiation. The IR spectra are recorded by FTIR spectrometer VARIAN 660-IR in the frequency range between 400 - 1400 cm^{-1} with a resolution of 2 cm^{-1}. X-ray photoelectron spectroscopy (XPS) measurements were carried out by spectrometer VG ESCALAB II using AlKα radiation with energy of 1486.6.eV. The binding energies were determined with an accuracy of ±0.1 eV utilizing the C_{1s} line at 285.0eV (from adventitious carbon) as a reference.

RESULTS AND DISCUSSIONS

Structural background

The studied materials are composed of three oxides: vanadium, titanium and phosphorus oxides, connected and forming various groups and units.

The phosphate atoms usually form a network consisting of PO_4 units linked with neighbouring PO_4 tetrahedra trough one-, two- or three P-O-P bridges (Bridging Oxygen BO), denoted as Q^i, where*i* is the number of the BO (n = 0, 1, 2 or 3) [7]. Linkage by two BO (Q^2 units) can be considered as PO_2^- middle groups in phosphate chains, while (Q^1) corresponds to PO_3^{2-} terminal units. Q^0 represents an isolated PO_4^{3-} tetrahedron known as orthophosphate unit. The vitreous P_2O_5 consists of Q^3 phosphate tetrahedra that form a three dimensional network. The addition of metal oxides results in "depolymerisation" of this network due to breaking of P-O-P bonds and

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creation of negatively charged non-bridging oxygen (NBO). The Q^i species change according to Kirkpatrick and Brow model [7, 8] in consecution $Q^3 \rightarrow Q^2 \rightarrow Q^1 \rightarrow Q^0$ with increasing of the amount of modifying oxide.

The vanadium atoms could be present in different oxygen environments forming various types of polyhedra as VO_6 octahedra, VO_5 groups (square pyramids or trigonal bi-pyramids) and VO_4 tetrahedra in the crystalline and amorphous vanadates [9-12]. In vanadate-phosphate systems mixed units are formed composed of VO_x and PO_4 polyhedra [12].

The TiO_2 in all polymorph forms is built from TiO_6 octahedra [13]. TiO_6 is the main structural unit in the titanium-phosphates as pyrophosphates [14], and NASICON (Na Super Ionic Conductor) like phosphates [15]. In the phosphate glasses Ti atoms are in six-, five- or fourfold coordination [16-18].

X-ray Diffraction

The broad halo in XRD patterns reveals the amorphous character of samples N1 and N2 with higher phosphate content (Fig. 1). The samples N3 and N4 are glassy-crystalline as defined from the diffraction peaks and the halo on diffractograms. The higher TiO_2 content (20 mol.%) is accountable for the appearance of pure rutile phase observed in the sample N4. An empty NASICON-type crystal structure was identified for crystalline part of sample N3 - $(TiO_2)_{10}(V_2O_5)_{60}(P_2O_5)_{30}$ as described in previous work [19]. The structural formula of NASICON-type vanadyl (V) titanium(IV) phosphate proposed by S. Titlbach et. al. [20] is $(V^VO)Ti^{IV}{}_6(PO_4)_9$.

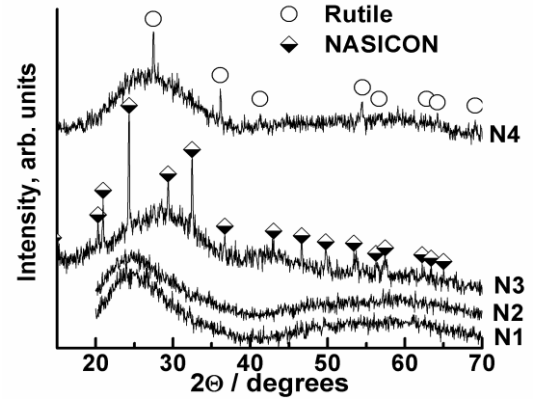

Fig. 1. XRD patterns of samples from $(TiO_2)_x(V_2O_5)_y(P_2O_5)_{100-x-y}$ system.

Infrared study

The infrared spectra of $(TiO_2)_x(V_2O_5)_y(P_2O_5)_{100-x-y}$ samples are presented in fig. 2. The absorption above 1200 cm^{-1} and the weak band at 1180cm^{-1} on the spectrum of sample N1 are connected with asymmetric and symmetric stretching of PO_2^- (Q^2) middle groups in phosphate chains [21]. The absence of a pronounced absorption peak at ~1250 cm^{-1} however demonstrates the formation of short chains. The bands at 1130cm^{-1} and 1064 cm^{-1} are due to vibrations of PO^- in PO_3^{2-} (Q^1) terminal groups in the phosphate chains and pyrophosphate units $P_2O_7^{4-}$, respectively [22, 23]. The P-O-P bridges absorb at ν_{as} ~ 900 cm^{-1} and ν_s ~ 740 cm^{-1}. The bands at the 940 cm^{-1} and 870-850 cm^{-1} are due to the symmetric and anti-symmetric stretching vibration of the VO_2 groups in the VO_4-polyhedra [9, 10]. The absorption at 1010 cm^{-1}might arise from stretching vibration of V=O vanadyl bond in VO_5-groups or/and normal mode of PO_4^{3-} (Q^0) isolated phosphate groups [24]. In the glass N1 probability to detect PO_4^{3-} unit is small, therefore more likely VO_5 and VO_4 units are present. With the increasing of the V_2O_5 content the absorption band at ~940 cm^{-1} disappeared and VO_4 units is not registered on IR spectrum of glass N2. The spectra of N3 and N4 are comparable: the absorption above ~1200 cm^{-1}, related to the PO_2^- phosphate groups, disappears and the band at 900 cm^{-1} shifts to lower (860 cm^{-1}) wavenumber due to mixed P-O-V bridge formation. This indicates that no phosphate chains in these samples exist and they are built of Q^1 and Q^0 species.

The IR spectrum of the glassy-crystalline sample N3 is similar to this of crystalline $NaTi_2(PO_4)_3$ [25,26] NASICON structure. The structure consists of TiO_6 octrahedra which share corners with six PO_4 tetrahedra while each PO_4 tetrahedron is connected by the corner with four TiO_6 octahedra [15]. As a results,isolated phosphate group PO_4^{3-} (Q^0), located at ~996 cm^{-1} and bending at 576 cm^{-1},as well as normal vibration of TiO_6octahedra ~at 640 cm^{-1} are identified in N3 spectrum. The band at 1020 $cm^{-1}$is due to V=O in VO_5 trigonal bipyramid.

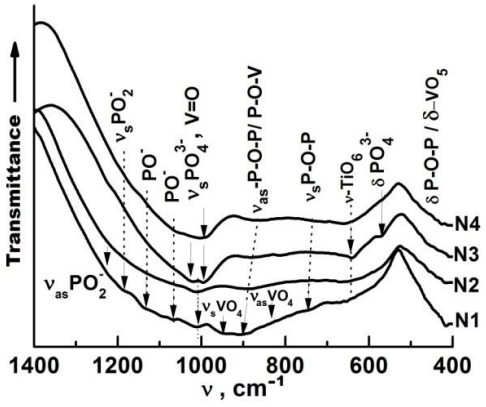

Fig. 2. Infrared spectra of samples $(TiO_2)_x(V_2O_5)_y(P_2O_5)_{100-x-y}$ system

The formation of TiO_2 Rutile phase leads to the higher concentration of P_2O_5in amorphous matrix, which reflect on the IR spectrum of sample N4 as shoulder located at 1060 cm^{-1} because of the appearance of additional PO_3^{2-} (Q^1) groups.

The bands in the 400 – 500 cm^{-1} range are due to the lattice vibrations in vanadium oxide network and deformation of PO_4 units.

X-ray Photoelectron spectroscopy investigation

The XPS spectra shown in Fig 3 (a-d) validate the existence of different structure units. The broad P2p high resolution spectra are deconvoluted in three $P2p_{3/2}$-$P2p_{1/2}$ doublets which correspond to Q^0 tetrahedra (PO_4^{3-}) at ~132.5 eV, Q^1 (PO_3^{2-}) at ~133.5 eV and (PO_2^-) Q^2 with binding energy (BE) around 134.5 eV [27, 28]. The dominance of pyro-phosphate groups $P_2O_7^{4-}$ is clearly visible. The number of isolated PO_4^{3-} phosphate group increases when the P_2O_5 content decreases (grow of component Q^o) whereas more PO_2^- units (Q^2) are detected at higher phosphate content.

O1s peak was deconvoluted in three components (Fig 3b): O1 with BE around 259-530.5 eV correspond to non-bridging oxygen (NBO) which forms oxygen bonds with titanium or vanadium and V-O-V bridges; O2 peak with BE=531-532 eV is assigned to mixed bridging bonds V-O-P and component O3 with BE of 533-534 eV associated with bridged oxygen in P-O-P bond or oxygen from adsorbed water [28].

The peak position of $Vp_{3/2}$ at ~517.6 eV (fig.3c) is evidence for predominantly V^{5+} valence of vanadium. The deconvolution with two components reveals weak asymmetry towards the lower energies due to the presence of V^{4+} with BE ≈ 516.5 eV.

Ti2p spectra on fig. 3(d) indicates the existence of Ti^{4+} valence state with BE($Ti2p_{3/2}$) ≈ 459.3 eV in the crystalline samples corresponding to Anatase/Rutile BE [29]. The BE of Ti in the glassy samples is shifted to higher values at 459.85 eV.

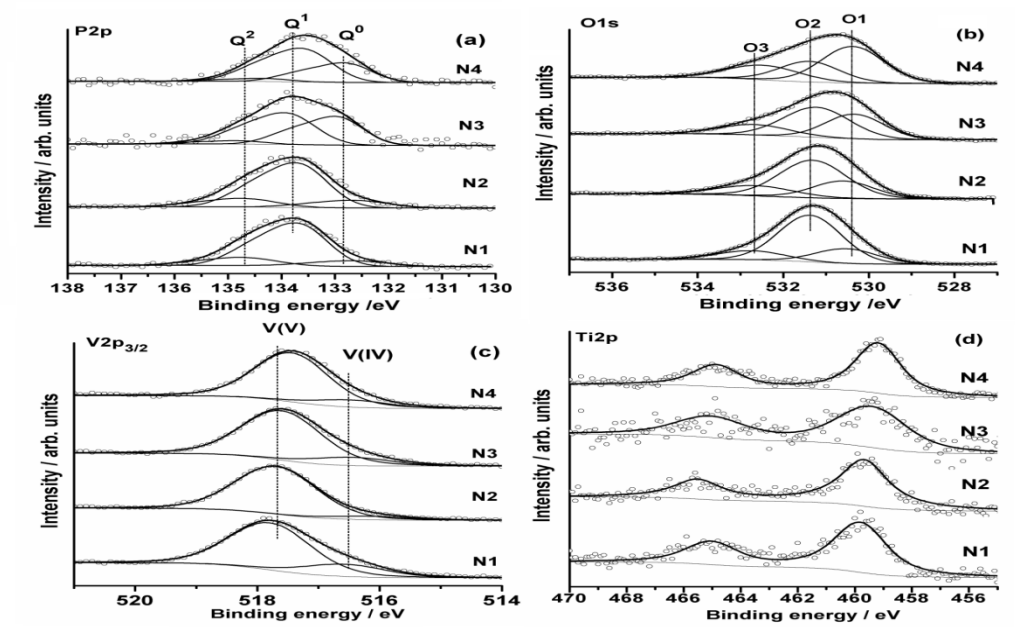

Fig. 3. High resolution X-ray photoelectron spectra of the $(TiO_2)_x(V_2O_5)_y(P_2O_5)_{100-x-y}$ samples: (a) P2p ; (b) O1s; (c) $V2p_{1/2}$; (d) Ti2p.

FTIR and XPS investigations show that pyrophosphate $(P_2O_7)^{4-}$ units are the major group in the samples under study. The units, however, are partially displaced by isolated PO_4^{3-} when the phosphorus content decreases or by PO_2^- units when the phosphate content grows.

The samples N3 and N4 are based on both: Q^1 with a two PO_3^{2-} tetrahedra connected in pyrophosphate units and Q^0, i.e. isolated PO_4^{3-} tetrahedra. The vanadium pentoxide plays role of the second glass former. Addition of V_2O_5 and/or TiO_2 leads to destroying P-O-P bridge structure introducing mixed P-O-V bridges and new NBOs. The titanium atoms possess stable fourth valence and octahedral coordination in all samples.

CONCLUSIONS

The study of materials from $(TiO_2)_x(V_2O_5)_y(P_2O_5)_{100-x-y}$ system reveals that the structure is characterized by different oxygen environment. The addition of V_2O_5 and TiO_2 leads to destroying P-O-P bridge structure introducing mixed P-O-V bridges and new NBOs. The

pyrohosphate ($P_2O_7^{4-}$) groups are the main structural units in the samples partially displaced by isolated PO_4^{3-}groups when the V_2O_5 and/or TiO_2 content increases or by PO_2^- units when the content of the transition metals decreases. The glass-crystalline samples with NASICON or Rutile type-structure possess lower P_2O_5 content.

The vanadium exist in two valence states V^{5+} and V^{4+}. The presence of VO_5 groups and TiO_6-octahedra is typical to all studied samples.

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REFERENCES

1. D. Vladikova, Z. Stoynov, G. Raikova, A. Thorel, A. Chesnaud, J. Abreu, M. Viviani, A. Barbucci, S. Presto, P. Carpanese, *Electrochim. Acta*, **56**, 7955 (2011).
2. R. V. Barde, S. A. Waghuley, J Advanced Ceramics, 2, 246 (2013).
3. B. Zhu, *Solid State Ionics*, **145**, 371 (2001).
4. Y. Daiko, *Journal of the Ceramic Society of Japan (JCS-Japan)*, **121**, 539 (2013)
5. Y. Jin, Y. Shen and Takashi Hibino, *Mater. Chem.*, **20**, 6214 (2010).
6. M.A. Moshareva, S.A. Novikova, A.B. Yaroslavtsev, *Inorg. Mater*., **52**, 1283 (2016).
7. R. K. Brow, *J. Non-Cryst. Solids*, **263&264**, 1 (2000).
8. R.K. Brow, C.A. Click, T.M. Alam, *J. Non-Cryst. Solids*, **274**, 9 (2000).
9. V.Dimitrov, *J. Non-Cryst. Solids*, **192&193**, 183 (1995).
10. Y. Dimitriev, V. Dimitrov, M. Arnaudov, and D. Topalov, *J. Non-Cryst. Solids*, **57**, 147 (1983).
11. M. Willinger, N. Pinna, D. S. Su, R. Schlögl, *Physical Review B*, **69**, 155114 (2004).
12. S. Boudin, A. Guesdon, A. Leclaire, M.-M.Borel, *Int. J. Inorg.Materials*, **2**, 561 (2000).
13. M. Matsui, M. Akaogi, *Molecular Simulation*, **6**, 239 (1991).
14. S. T. Norberg, G. È. Svensson and J. È. Albertsson, *Acta Cryst.*, **C57**, 225 (2001).
15. S. Benmokhtar, A. El Jazouli, A. Aatiq, J.P. Chaminade, P. Gravereau, A. Wattiaux, L. Fourne`s, J.C. Grenier, *J. Solid St. Chem*., **180**, 2004 (2007).
16. A. Tang, T. Hashimoto, T. Nishida, H. Nasu, K. Kamiya, *Journal of Ceramic Society of Japan*, **112**, 496 (2004).
17. B. Tiwari, A. Dixit, G. P. Kothiyal, M. Pandey, S. K. Deb, *BARC Newsletter*, **285**, 167 (2007).
18. S. Lee, H. Maeda, A. Obata, K. Ueda, T. Narushima, T. Kasuga, *J. Non-Cryst. Solids*, **426**, 35 (2015).
19. D. V. Blaskova-Kochnitcharova, T. Petkova , L. Fachikov, E. Lefterova , I. Kanazirski, P. Angelov, S. Vassilev, *Bulg. Chem. Commun*., **45:A**, 159 (2013).
20. S. Titlbach, W. Hoffbauer, R. Glaum, *J. Solid State Chem*., **196**, 565 (2012).
21. L. L. Velli, C. P. E. Varsamis, E. I. Kamitsos, D. Möncke& D. Ehrt, *Phys. Chem. Glasses*, **46**, 178 (2005).
22. A. Shaim, M. Et-tabirou, *Materials Chemistry and Physics*, **80**, 63 (2003).
23. K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds: Part A: Theory and Applications in Inorganic Chemistry, Sixth Edition John Wiley & Sons, Inc., 2009
24. H-K Roh, M-S Kim, K. Chung, M. Ulaganathan, V. Aravindan, S. Madhavi, K. Roh, K-B Kim, *Journal of Materials Chemistry A*, **5**, 17506 (2017).
25. P. Tarte, A. RulmontAnd C. Merckaert-Ansay, *Spectrochimica Acta*, **42A**, 1009 (1986).
26. R. Gresch, W. Muller-Warmuth, H. Dutz, *J. Non-Cryst. Solids*, **34**, 127 (1979).
27. A. V. Naumkin, A. Kraut-Vass, S. W. Gaarenstroom, C. J. Powell, NIST Standard Reference Database 20, Version 4.1 (2013), http://srdata.nist.gov/xps
28. A. Majjane, A.Chahine, M. Et-tabirou, B. Echchahed, T. Do, P. Mc Breen, *Mater. Chem. Phys*., **143**, 779 (2014).
29. U. Diebold, T. E. Madey, *Surf. Sci. Spectra*, **4**, 227 (1996).

МОДИФИЦИРАНЕ НА МРЕЖАТА НА ФОСФАТНИ МАТЕРИАЛИ ЧРЕЗ ДОТИРАНЕ С ПРЕХОДНИ МЕТАЛИ

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(Резюме)

Тази работа се фокусира върху изследването на структурните промени на фосфатните материали при дотиране с оксиди на преходните метали. Структурата на новите композити $(TiO_2)_x(V_2O_5)_y(P_2O_5)_{100-x-y}$ се разглежда по отношение на състава, структурните единици и валентността. За анализ на материалите се използват Ренгенова дифракция, ИЧ и фотоелектронна спектроскопия. Добавянето на V_2O_5 и TiO_2 разрушава P-O-P мостовата структура и води до образуване на смесени и немостови кислородни връзки, както и до появата на изолирани PO_4^{3-} единици. При високо съдържание на преходните метали са получени стъклокристални образци.

Ключови думи: оксиди на преходни метали, структурни изследвания, IR, XPS