

THE SYNTHESIS AND PROPERTIES OF THE PHASES OBTAINED BY SOLID-SOLID REACTIONS

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Dedicated to Prof. Ing. Jaroslav Šesták, DrSc. at the occasion of his 70th birthday

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Abstract

The presented work encompasses the subject of the studies and the results obtained over the last years by the research workers of the Department of Inorganic Chemistry. They include mainly the studies on the reactivity of metal oxides, searching for new phases in binary and ternary systems of metal oxides as well as describing phase relations establishing in such systems. They also encompass works on the extensive characteristics of physico-chemical properties of the newly obtained compounds.

Keywords: reactivity of oxides, phase equilibria, XRD, DTA

1. Introduction

A great majority of technological processes is conducted either in the solid phase or with the participation of that sort of phases. That encompasses all the metallurgical processes, the technologies of obtaining ceramic or refractory materials or cements, the processes conducted with the

participation of contact catalysts, as well as the cutting-edge technologies. These include the ones of obtaining ceramic conductors and superconductors, semiconductors, laser materials or nanomaterials. Hence extensive research on the whole range of solid-state chemistry is carried out, including both the basic as well as technological works.

At the Institute of Inorganic Chemistry of

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the Department of Inorganic and Analytical Chemistry of the Faculty of Technology and Chemical Engineering at Szczecin University of Technology, basic studies relating to solid-state chemistry, initiated by the late Professor Jadwiga Walczak and the late Professor Maria Kurzawa, have been conducted. The results of the studies may comprise the basis in designing new catalysts of industrial processes or new materials demonstrating specific thermal, optical, electrical or chemical properties.

2. Experimental

A number of research methods in solving the raised problems have been employed, among which the following methods: the XRD analysis (DRON-3, Bourestnik, Russia), differential thermal analysis (DTA/TG) (F. Paulik – L. Paulik – L. Erdey derivatograph, MOM, Budapest or SDT 2960 apparatus of TA Instruments or the TGA/SDTA 851, Mettler Toledo, USA and IR spectroscopy (SPECORD M 80, Carl Zeiss, Jena, Germany) are the most fundamental ones. With the view to characterizing the new compounds in the most extended way, there have been works conducted in cooperation with other domestic and foreign centers. The works include the research carried out with the use of such methods as: EPR, NMR, XPS, Mössbauer spectroscopy as well as the magnetochemical, neutronographical, electrical methods and luminescent spectra.

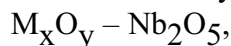
3. Results

In recent years intensive studies regarding the structure of the compounds formed in the

series of binary oxide systems, such as: $M_xO_y - Nb_2O_5$, where $M = Mg, Ni, Co, Zn, Al, Fe, Cr, Ga, Ti, W$ and Mo , have been carried out. Also the works connected with the formation of new compounds and phase relations establishing in a few ternary oxide systems, i.e. $V_2O_5 - MoO_3 - \alpha-Sb_2O_4$, $V_2O_5 - Cr_2O_3 - \alpha-Sb_2O_4$, $MO - V_2O_5 - Fe_2O_3$ where $M = Co, Mg, Zn$, $MO - In_2O_3 - V_2O_5$, where $M = Mg, Zn, Co$, $MO - V_2O_5 - Cr_2O_3$, where $M = Mg, Ni$, were continued. Moreover, reciprocal reactivity of selected tungstates (VI) of rare earths metals RE_2WO_6 with the tungstates (VI) of d-electron metals MWO_4 has been studied.

Also, the ternary systems of the following oxides $MO - V_2O_5 - MoO_3$, where $M = Co, Zn$, were investigated with the view to finding the compounds meeting the criteria which are required from ecological pigments. The compounds constituting these systems are regarded as friendly or accepted by environment elements. The components of these systems have been recognized in ceramic industry as raw materials for years.

The data provided in literature suggest that in all the binary systems:



where $M = Mg, Ni, Co, Zn, Al, Fe, Cr, Ga, Ti, W$ and Mo , the phases of the double crystallographic shear type are formed, in the structure of whose the ReO_3 type blocks can be distinguished, built from the regular octahedra MO_6 , linked by their corners.

Individual blocks are connected by edge-sharing. In this way a specific block structure is formed, the structure within which two reciprocally perpendicular systems of shear

planes occur. The width and height of the blocks are described by the n and m parameters corresponding to the number of octahedra linked by corners between the neighbouring shear planes, however their length may be infinitely large ($n \times m \times \infty$). The presence of two sets of shearing planes makes it possible for a great number of intermediate phases, which often differ insignificantly one from another in the chemical content, but still can be distinguished with the help of the XRD method, to be formed. The presence of the ReO_3 type blocks, distinctly limited in two dimensions ($n \times m$) and demonstrating infinite expansion in the third dimension, in the phases of the double crystallographic shear structure, may be a cause of the clearly pointed out anisotropy of the physical properties of these compounds.

The research on the thermal expansion of a large number of structurally diversified group of compounds of the double crystallographic shearing type, conducted at the Institute of Inorganic and Analytical

Chemistry, confirmed the earlier presented speculation that these phases are characterized by strongly indicated thermal expansion anisotropy. In the case of the $\text{Nb}_{14}\text{Mo}_3\text{O}_{44}$ and $\text{Nb}_{12}\text{Mo}_3\text{O}_{33}$ phases, the mean linear coefficients of thermal expansion very rarely exhibited negative values towards the crystallographic axis, connected with the shortest parameter of a unit cell [1,2].

The studies on the ternary system of oxides $\text{V}_2\text{O}_5 - \text{MoO}_3 - \alpha\text{-Sb}_2\text{O}_4$, permitted, among others, to establish that two new phases, i.e. the $\text{Sb}_3\text{V}_2\text{Mo}_3\text{O}_{21}$ compound and a substitute solid solution MoO_3 in SbVO_5 , are formed in this system in air atmosphere [3,4]. The solubility limit of MoO_3 in SbVO_5 is at least 17.50 and does not exceed 20,00% mol MoO_3 in the oxides' initial mixture. This solution is formed by incorporating the Mo^{6+} ions in the crystal lattice of SbVO_5 , supplanting the V^{5+}

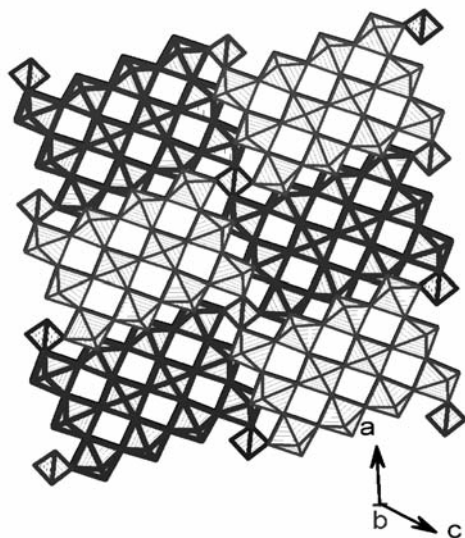


Fig. 1. The structure of $\text{Nb}_{12}\text{Mo}_3\text{O}_{33}$

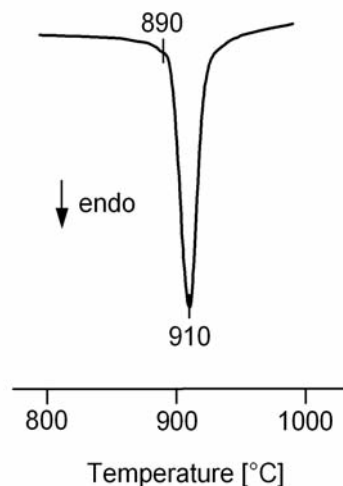
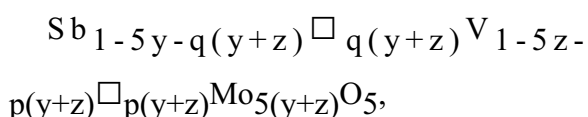


Fig. 2. The DTA curve of NbVSb_{7+x}

or/and Sb^{5+} ions. The compensation of the redundant positive charge is conducted by the formation of an equivalent number of cation vacancies supplanting the V^{5+} or/and Sb^{5+} ions. It was demonstrated that the solid solution MoO_3 in SbVO_5 depicts the homogeneity area [4], which in air atmosphere, in the $\text{V}_2\text{O}_5 - \text{MoO}_3 - \alpha\text{-Sb}_2\text{O}_4$ system can be described by the generalized formula:



where: $q+p = 1$, $5y$ = the number of Mo^{6+} ions built in into the crystal lattice of SbVO_5 , replacing Sb^{5+} , $5z$ = the number of Mo^{6+} ions replacing V^{5+} , $q(y+z)$ = the number of cation vacancies, substituting Sb^{5+} , $p(y+z)$ = the number of cation vacancies supplanting V^{5+} and $0 < y+z \leq 0,0208$.

Electrical studies on the mono-phase preparations containing the solid solution of MoO_3 in SbVO_5 , conducted within the framework of cooperation with the Department of Crystal Physics in the Institute of Physics at Silesian University, within the range of temperatures from 80 up to 500 K, demonstrated that at low temperatures the phases are insulators, whereas at high – the semi-conductors of the p type [5]. The measurements of the phases' electrical resistance in the temperature function revealed consecutively the minimum and maximum of its value that was changing by 7 orders of magnitude around room temperature. The p type of these phases' conduction seems to be related to the

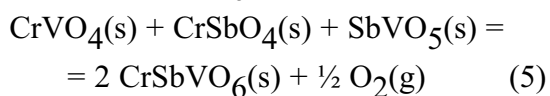
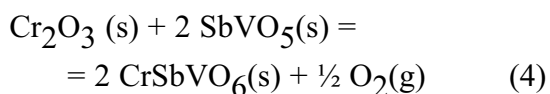
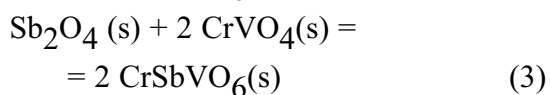
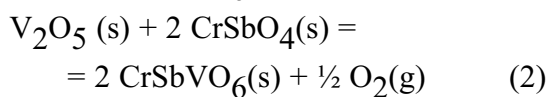
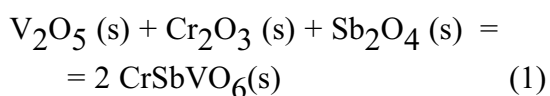
presence of cation vacancies being formed where the V^{5+} or/and Sb^{5+} ions previously were or during the formation of the solid solution of MoO_3 in SbVO_5 . The gigantic electrical resistance peak may indicate that the metal-insulator phase transition, the so-called Mott transition, took place in the studied phases. In oxide phases, transition of this kind occurs relatively rarely and it was discovered in V_2O_3 at the temperature of 150 K, for the first time. Phases demonstrating such electrical properties may find application in electrical appliances of great power as the temperature controlled electric current switches. The lack of mechanical contacts, where sparking takes place and a great amount of heat is released, is an advantage of such switch. It plays a significant role e.g. in appliances used in coal mines, where methane hazard occurs.

At present further research is being conducted, aimed at explaining the mechanisms of the occurrences of such enormous changes of electrical resistance in temperature function, in the phases of the solid solution of MoO_3 in SbVO_5 .

The results of the research on the ternary oxide system of $\text{V}_2\text{O}_5 - \text{Cr}_2\text{O}_3 - \alpha\text{-Sb}_2\text{O}_4$, have demonstrated that a CrSbVO_6 compound, learned about only recently, is formed in this system [6]. The literature data inform that phases of the solid solutions type, with the formulas: $\text{Cr}_1\text{V}_x\text{Sb}_1\text{O}_{4+2x}$ and $\text{CrV}_x\text{Sb}_{1+x+2z}\text{O}_{4+4x+4z}$ where $0 < x < 1$, exist in this system [7,8]. Studies on the catalysts, which contain both the CrSbVO_6 compound as well as solid solutions, have demonstrated that these catalysts are active and highly selective in the processes of

obtaining acrylonitrile directly from propane [7]. This fact plays an important role in designing the new class catalysts of this process. Generating acrylonitrile from propane, and not as before from propylene, will lower the costs of its obtaining by circa 20% [9]. The authors of this work have obtained the phases of the solid solutions type by means of the precipitating method from alcoholic solutions containing SbCl_5 , $\text{VO}(\text{C}_5\text{H}_7\text{O}_2)_2$ and $\text{Cr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ [7].

The CrSbVO_6 compound was obtained as a result of a reaction conducted in the solid phase, in air, between various substrates in accordance with the reaction equations [6]:



In the course of the conducted studies it was established that the CrSbVO_6 compound melts incongruently at the temperature of 1300°C with the solid Cr_2O_3 being released. Indicating the powder diffraction pattern of the CrSbVO_6 compound confirmed that it crystallizes in the tetragonal system and has the rutile type structure. The calculated unit cell's parameters are: $a = b = 0,45719(12)$ nm, $c = 3,0282(8)$ nm. The number of particles in the

unit cell is $Z = 2$.

The preliminary study of phase relation in the ternary oxide system $\text{V}_2\text{O}_5 - \text{Nb}_2\text{O}_5 - \text{Sb}_2\text{O}_4$ in the air atmosphere have shown that in the system the new compound is formed. This compound with formula NbVSbO_{7+x} , where $0 < x \leq 0.5$ has been obtained both from oxides: Nb_2O_5 , V_2O_5 , α - Sb_2O_4 and from a mixture comprising SbVO_5 and Nb_2O_5 . The NbVSb_{7+x} is stable up to 890°C [10]. The DTA curve of NbVSb_{7+x} showed in the Figure 2.

As a result of the reactions taking place in the solid state of concentration in the $\text{MO} - \text{V}_2\text{O}_5 - \text{Fe}_2\text{O}_3$ ($M = \text{Co}, \text{Mg}, \text{Zn}$) system, a series of the not known before phases, that is $\text{M}_3\text{Fe}_4\text{V}_6\text{O}_{24}$ ($M = \text{Mg}, \text{Zn}$) [11], $\text{Co}_{2.616}\text{Fe}_{4.256}\text{V}_6\text{O}_{24}$ [12] and $\text{M}_2\text{FeV}_3\text{O}_{11}$ ($M = \text{Co}, \text{Mg}, \text{Zn}$), has been obtained [13]. The results of the studies conducted in cooperation with the research staff of the Institute of Physics of Szczecin University of Technology, indicate that the magnetic properties of these phases change depending on the way of their synthesis, particularly on their heat treatment. This dependency is most probably related to the structure, i.e. the case of the disordered state of cations in the crystal lattice. Oxygen deficit resulting from the possibility of vanadium to occur in various oxidation states, may play an equally significant role. Both the disordered state and oxygen deficit may change under the influence of temperature, which causes the change of magnetic properties [14].

In different studies complete phase equilibrium diagrams of the $\text{NiO} - \text{V}_2\text{O}_5 -$

Cr_2O_3 and $\text{MgO} - \text{V}_2\text{O}_5 - \text{Cr}_2\text{O}_3$ systems to the solidus line were prepared (Fig.2,3) [15].

Within the scope of interest in the

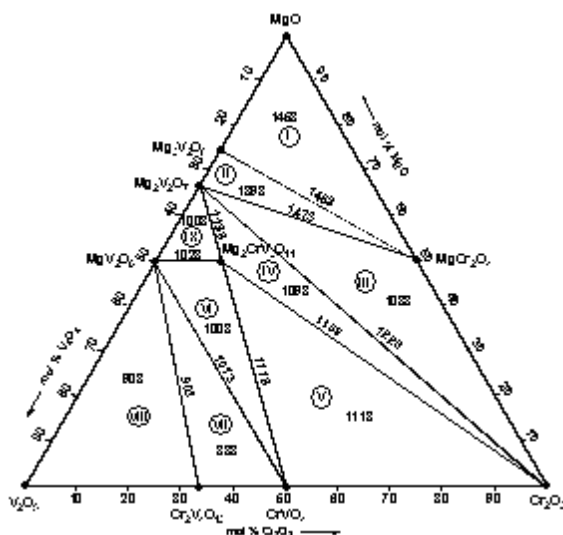


Fig. 3. The phase diagram of $\text{MgO} - \text{V}_2\text{O}_5 - \text{Cr}_2\text{O}_3$ system in the solid state

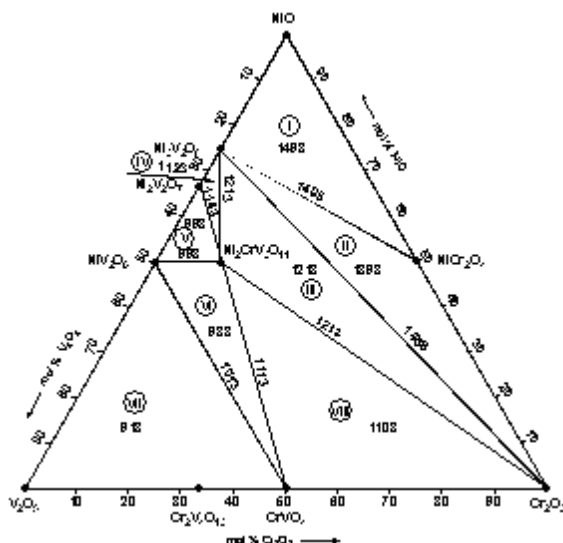


Fig. 4. The phase diagram of $\text{NiO} - \text{V}_2\text{O}_5 - \text{Cr}_2\text{O}_3$ system in the solid state

Department of Inorganic Chemistry remain, among others, the oxide systems: $\text{MO} - \text{In}_2\text{O}_3 - \text{V}_2\text{O}_5$, where $\text{M} = \text{Mg}, \text{Zn}, \text{Co}$. The latest research reveals that as a result of a reaction in the solid phase between $\text{M}_2\text{V}_2\text{O}_7$ and InVO_4 , where $\text{M} = \text{Mg}, \text{Zn}$ and Co , compounds with the generalized formula $\text{M}_2\text{InV}_3\text{O}_{11}$ are formed [16, 17].

These compounds crystallize in the triclinic system and are isostructural with $\text{GaMg}_x\text{Zn}_{2-x}\text{V}_3\text{O}_{11}$ [18]. VO_4 tetrahedra and VO_5 trigonal bipyramids can be isolated in the structures of these compounds [18]. The initial structural research implies that these compounds may find application as photocatalysts.

The research on ternary systems:

$\text{MO} - \text{V}_2\text{O}_5 - \text{MoO}_3$, where $\text{M} = \text{Co}, \text{Zn}$ conducted in the Department of Inorganic and Analytical Chemistry demonstrated that the reaction of $\text{M}_3\text{V}_2\text{O}_8$ with MMoO_4 resulted in the formation of compounds with the $\text{M}_{2.5}\text{VMoO}_8$ formula. The chromaticity coordinates in the colour space CIELAB of the new compounds were determined. The $\text{Co}_{2.5}\text{VMoO}_8$ compound is characterized by the green colour and $\text{Zn}_{2.5}\text{VMoO}_8$, yellow. In the next stage of the research, part of the Co^{2+} ions in the $\text{Co}_{2.5}\text{VMoO}_8$ compound were supplanted by the Mg^{2+} or Zn^{2+} ions, which resulted in obtaining the following compounds:

$\text{CoMg}_{1.5}\text{VMoO}_8$ and $\text{CoZn}_{1.5}\text{VMoO}_8$.

Tests of the applicability of all the obtained compounds as ceramic pigments in low-temperature borate-silicate glazes, commonly used in ceramic industry, were conducted. The tests revealed that these

compounds meet the conditions which ceramic pigments must comply with. The $\text{Co}_{2.5}\text{VMoO}_8$, $\text{CoMg}_{1.5}\text{VMoO}_8$ and $\text{CoZn}_{1.5}\text{VMoO}_8$ compounds give all the tested glazes (depending on the combination: the kind of the glaze, amount and the type of the pigment) the colour from dark blue to light blue. The obtained coatings were characterized by good quality. The $\text{Zn}_{2.5}\text{VMoO}_8$ compound gives the glazes the colour from light cream to cream white.

All the compounds used as pigments demonstrate very good coating qualities. These compounds give the glaze the colour, while depicting very low pigment content (1–5%). $\text{Zn}_{2.5}\text{VMoO}_8$, particularly, owing to its good coating qualities may be a valuable, environment friendly pigment [19].

The compounds of rare earths are well-known as multi-functional materials exhibiting unique physico-chemical properties. These compounds find their application mainly as luminescent materials, which practically do not require any kind of energy as a spectrochemical source. Inorganic phosphoruses are commonly used for the manufacturing of radiation detectors of different wavelength, solid body lasers, LCD monitors and fluorescent lamps and cathode-ray tubes [20]. Moreover, the compounds containing the metals of rare earths demonstrate interesting magnetic properties.

The research conducted at the Department of Inorganic and Analytical Chemistry, and relating to the reciprocal reactivity of selected tungstates (VI) of rare earths (RE_2WO_6) with the tungstates (VI) of d-electron metals (MWO_4) revealed that these compounds interact in air atmosphere,

forming the following families of isostructural compounds:

- $\text{ZnRE}_4\text{W}_3\text{O}_{16}$, where RE = Y, Nd, Sm, Eu, Gd, Dy i Ho [21],
- $\text{Co}_2\text{RE}_2\text{W}_3\text{O}_{14}$ and $\text{CoRE}_4\text{W}_3\text{O}_{16}$, where RE = Sm, Eu i Gd [22],
- $\text{CoRE}_2\text{W}_2\text{O}_{10}$, where RE = Y, Dy, Ho i Er [23],
- $\text{Cu}_3\text{RE}_2\text{W}_4\text{O}_{18}$, and $\text{CuRE}_2\text{W}_2\text{O}_{10}$ where RE=Nd, Sm, Eu i Gd [24],
- $\text{Cu}_3\text{RE}_2\text{W}_4\text{O}_{18}$, where RE = Dy, Ho i Er,
- $\text{CdRE}_2\text{W}_2\text{O}_{10}$, where RE = Y, Nd, Sm, Eu, Gd, Dy, Ho i Er,
- $\text{NiRE}_2\text{W}_2\text{O}_{10}$, where RE = Nd, Sm, Eu, Gd,
- $\text{NiRE}_2\text{W}_2\text{O}_{10}$, where RE = Dy, Ho i Er,
- $\text{MPr}_2\text{W}_2\text{O}_{10}$, where M = Mn, Co i Cd,
- $\text{MPr}_2\text{W}_2\text{O}_{10}$, where M = Ni, Cu i Zn.

The obtained compounds demonstrate thermal stability in a wide range of temperatures. They decompose in the solid state or melt at temperatures, in most cases, higher than 1100°C, and some of them even above 1300°C. The IR tests point to a very complicated structure of the obtained phases. In the structure of many of them one can distinguish isolated polyanions $(\text{W}_4\text{O}_{16})^{8-}$ or $[(\text{W}_2\text{O}_9)^{6-}]^\infty$, which were created by connecting the WO_6 regular octahedra by means of oxygen bridges. It was found that among the obtained compounds, particularly those which contain the Eu^{3+} ions, depict strong luminescence. Thus, they can be used as luminescent materials.

Congratulations and the best wishes form all research workers from Department of Inorganic and Analytical Chemistry to Professor Jaroslav Šesták on the occasion of his 70th birthday.

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