DTA/TG, IR, EPR and XPS studies of some praseodymium(III) tungstates

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1. Introduction

The trivalent metal molybdates and tungstates include a number of materials with interesting fluorescent, laser, piezoelectric, ferroelectric and ferroelastic properties. The special group of these compounds is family of rare-earth metal molybdates and tungstates. These compounds adopt a large number of different polymeric structures and many of them display negative thermal expansion. In the Pr$_2$O$_3$–WO$_3$ system, the following praseodymium(III) tungstates are known: Pr$_2$(WO$_4$)$_3$ (Pr$_2$O$_3$:WO$_3$ – 1:3); Pr$_2$W$_2$O$_9$ (1:2); Pr$_2$W$_5$O$_{27}$ (4:5); Pr$_2$WO$_6$ (1:1); Pr$_6$W$_2$O$_{15}$ (3:2) and probably Pr$_8$W$_5$O$_{27}$ (4:5) [6,7]. The praseodymium(III) tungstate (Pr$_2$WO$_6$), belonging to the family of isostructural compounds RE$_2$W$_2$O$_6$ (RE = Ce–Gd), shows polymorphism [6,7]. The low-temperature polymorphic modification (II-Pr$_2$WO$_6$) crystallizes in the monoclinic system (the space group C2/c) and has the following parameters of the unit cell: a = 1.6691 nm; b = 1.4436 nm; c = 0.5546 nm; β = 107.54° [6,8]. Deformed, isolated trihedral bipyramids, WO$_6$, and three deformed, non-equivalent PrO$_6$ cubes are observed in the structure of this modification [6] (Fig. 2). The high-temperature form (V-Pr$_2$WO$_6$) crystallizes in the orthorhombic system with the lattice constants: a = 0.5394 nm; b = 0.9274 nm; c = 1.0241 nm [6]. The polymorphic transition of II-form to V-modification occurs at 1823 K [7]. Pr$_2$WO$_6$ melts incongruently at 1948 K [6].

In this paper, we completed the previous experimental data related with thermal properties of Pr$_2$WO$_6$. Particularly, we have studied and analyzed EPR and XPS spectra of the II-Pr$_2$WO$_6$ and II-Pr$_2$W$_2$O$_9$ phases.

2. Experimental

2.1. Sample preparation

Polycrystalline samples of Pr$_2$W$_2$O$_9$ and Pr$_2$WO$_6$ were prepared by the solid-state reaction according to the following equations:

Pr$_2$O$_{11+3W}$(s) $\rightarrow$ 3Pr$_2$W$_2$O$_9$(s) + O$_{2(g)}$  
(1)

Pr$_2$O$_{11+3W}$(s) $\rightarrow$ 3Pr$_2$WO$_6$(s) + O$_{2(g)}$  
(2)

The reagents (Pr$_6$O$_{11}$, 99.9% Aldrich; WO$_3$, 99.9% Fluka) were weighed in appropriate ratios and ground in an agate mortar. The obtained mixtures were heated in the air in the following cycles: 1073 K (12 h); 1173 K (12 h); 1273 K (12 h) and 1323 K (12 h). For better reactivity, the Pr$_6$O$_{11}$/WO$_3$ mixtures were ground in an agate mortar after each 12-h period of annealing. The XRD measurements of the samples obtained after
the last heating cycle of Pr$_6$O$_{11}$/6WO$_3$ and Pr$_6$O$_{11}$/3WO$_3$ mixtures have shown that they contain only II-Pr$_2$W$_2$O$_9$ and II-Pr$_2$WO$_6$, respectively.

2.2. Measurements

Powder X-ray diffraction patterns were collected within the range from 10$^\circ$ to 52$^\circ$ 2θ with a step 0.02$^\circ$ 2θ and counting time 1 s per step on a DRON-3 diffractometer with Cu Kα radiation (λ = 0.15418 nm).

DTA-TG studies were performed on a TA Instruments thermoanalyzer (Model SDT 2960) at the heating or cooling rate of 10 K min$^{-1}$ to the maximum temperature of 1773 K and in the air and an inert atmosphere (nitrogen, 99.996%) with the gas flow 110 mL h$^{-1}$.

Infrared spectral data were collected on a Specord M80 spectrophotometer in the range of 300–1200 cm$^{-1}$ using KBr pellets.

EPR spectra were recorded on a conventional X-band Bruker ELEXSYS E 500 CW-spectrometer operating at 9.5 GHz with 100 kHz magnetic field modulation. The investigated samples were in fine powder form. The first derivative of the powder absorption spectra has been recorded as a function of the applied magnetic field. Temperature dependence of the EPR spectra of the powder sample in the 90–300 K temperature range was recorded using an Oxford Instruments ESP nitrogen-flow cryostat.

XPS studies were carried out with use of the Prevac electron spectrometer, equipped with SES 2002 (VG Scienta) electron energy analyzer working in Constant Energy Aperture mode. Samples were excited with Mg Kα radiation. The spectra were acquired with pass energy of 50 eV. Calibration of the energy scale was done prior to analysis basing on Ag 3d transition. A shift of XPS lines due to the charging of the surface was observed and it was corrected numerically during analysis of the spectra. It was assumed that carbon C 1s line should be placed at 284.6 eV (adventitious carbon) and the positions of other XPS lines were shifted accordingly.

3. Results and discussion

3.1. XRD and DTA–TG studies

Fig. 3 shows XRD patterns of the II-Pr$_2$W$_2$O$_9$ and II-Pr$_2$WO$_6$ phases. The position and relative intensity of each diffraction line recorded on X-ray powder diffraction patterns of low polymorphic modification of Pr$_2$W$_2$O$_9$ as well as II-Pr$_2$WO$_6$ are in very good accordance with the suitable data for these phases reported by the International Centre for Diffraction Data [9].

Figs. 4 and 5 show DTA and TG curves of Pr$_2$W$_2$O$_9$, recorded during heating of this compound in two different atmospheres. The first endothermic effect with its onset at 1389 K (nitrogen atmosphere, Fig. 5) or at 1390 K (air, Fig. 4) not associated with mass change of the samples, corresponds to a polymorphic transition of II-Pr$_2$W$_2$O$_9$ to I-Pr$_2$W$_2$O$_9$. These values of transition temperature
Fig. 4. DTA–TG curves of Pr$_2$W$_2$O$_9$ (air atmosphere).

Fig. 5. DTA–TG curves of Pr$_2$W$_2$O$_9$ (nitrogen atmosphere).

are close to the value obtained earlier [7]. This transformation is associated with a change of crystallographic structure of Pr$_2$W$_2$O$_9$ (monoclinic II-Pr$_2$W$_2$O$_9$ → cubic I-Pr$_2$W$_2$O$_9$). The second endothermic effect recorded on the DTA curve of Pr$_2$W$_2$O$_9$ at 1461 K (N$_2$ atmosphere, Fig. 5) or at 1462 K (air, Fig. 4) is connected with incongruent melting of Pr$_2$W$_2$O$_9$. No mass loss associated with this endothermic effect was observed on the TG curves recorded during DTA–TG studies made in different atmospheres (Figs. 4 and 5). The process of incongruent melting can be described by the following equation:

$$\text{Pr}_2\text{W}_2\text{O}_9(s) \leftrightarrow \text{Pr}_8\text{W}_5\text{O}_{27}(s) + \text{liquid}$$

Melting manner of Pr$_2$W$_2$O$_9$ confirms the third endothermic effect appearing on the DTA curve of this compound at 1630 K (air, Fig. 4) or at 1636 K (nitrogen atmosphere, Fig. 5). This effect is associated with incongruent melting of Pr$_8$W$_5$O$_{27}$ [6]. The mass loss connected with the evaporation of liquid and corresponding only to the third endothermic effect was observed on the both TG curves (Figs. 4 and 5).

Fig. 6 shows DTA curves of Pr$_2$W$_2$O$_9$ recorded in air as well as in inert atmosphere during heating this phase up to 1433 K and DTA curves recorded during controlled cooling down to 1073 K. The exothermic effect with its onset at 1384 K (inert atmosphere,

Fig. 6A) or at 1386 K (air, Fig. 6B) is connected with crystallization of a low-temperature form of Pr$_2$W$_2$O$_9$. It means that the polymorphic transition of II-Pr$_2$W$_2$O$_9$ to I-Pr$_2$W$_2$O$_9$ is reversible. On the DTA curve of Pr$_2$WO$_6$ (not presented here) any effects were recorded up to 1773 K.

3.2. IR spectra

Fig. 7 shows IR spectra of II-Pr$_2$W$_2$O$_9$ (spectrum A) and II-Pr$_2$WO$_6$ (spectrum B). IR spectrum of II-Pr$_2$W$_2$O$_9$ shows a big similarity to the infrared spectrum of this compound previously recorded by other authors [10]. Based on the literature information
Fig. 7. IR spectra of II-Pr$_2$W$_2$O$_9$ (A) and II-Pr$_2$WO$_6$ (B).

The absorption band recorded for II-Pr$_2$W$_2$O$_9$ with the maximum at 868 cm$^{-1}$ is due to the stretching modes of W–O bonds in joint WO$_6$ octahedra forming the structure elements [(W$_2$O$_9$)$_6$$^-$$^\infty$]. The several absorption bands in the 804–508 cm$^{-1}$ region can be assigned to the asymmetric stretching vibration of W–O bonds in joint WO$_6$ octahedra and also to the oxygen double bridge bonds WOOW [10]. The absorption bands below 500 cm$^{-1}$ can be assigned to the symmetric and also asymmetric deformation modes of W–O bonds as well as to the deformation modes of the oxygen bridges WOOW [9]. The II-Pr$_2$WO$_6$ spectrum has not yet been presented in a literature. This spectrum shows a big similarity to the IR spectra of other isostructural rare-earth metal tungstates RE$_2$WO$_6$ [11]. The absorption band with its maximum at 872 cm$^{-1}$ can be due to the stretching modes of W–O bonds in isolated trihedral bipyramides WO$_5$ [11]. The absorption bands at 760 and 686 cm$^{-1}$ can be assigned to the asymmetric stretching modes of W–O bonds in WO$_5$. Several absorption bands with their maxima recorded below 600 cm$^{-1}$ can be due to the deformation modes of W–O bonds in WO$_5$ [11].

3.3. EPR spectra

A group of II-Pr$_2$W$_2$O$_9$ and II-Pr$_2$WO$_6$ powders investigated by using the EPR technique revealed existence of the X-band weak resonance signal in whole temperature range up to 300 K. The EPR results are shown in Fig. 8. The shape of the EPR lines is the same for both powders and consists mainly of one sharp line with $g = 2.07$ (Fig. 8a), although the line seem to be a superposition of at least two different lines. The position of the first line, centered at $g = 2.07$ changes with a temperature over 60 K suggesting the presence of some internal magnetic field in the sample. About 17 K there clearly arise second type line in the EPR spectrum, centered at about $g = 2.75$ (Fig. 8b). It leads to a complex behaviour of a temperature dependence of a total integrated intensity. EPR integrated intensity, $\chi_{\text{EPR}}$, is calculated as an area under the absorption EPR spectrum and is usually proportional to the magnetic susceptibility of the investigated spin system. From our investigations it results that the Curie–Weiss law applied to the integrated intensity is satisfied only in the temperature range below 17 K. The least-square fitting of the experimental points to the Curie–Weiss law produced $T_{\text{CW}} = 4$ K for II-Pr$_2$WO$_6$ sample and $T_{\text{CW}} = 0.3$ K for II-Pr$_2$W$_2$O$_9$ sample indicating on a weak ferromagnetic interaction between paramagnetic ions. It was confirmed also by a shape of $\chi_{\text{EPR}} \times T$ dependence on a temperature. In general, this product is proportional to the square root of an effective magnetic moment. For the II-Pr$_2$WO$_6$ and II-Pr$_2$W$_2$O$_9$ the effective magnetic moment decreases with temperature decrease in high-temperature range ($T > 60$ K), but increases in low-temperature range below 17 K for II-Pr$_2$WO$_6$ and stay close to zero for II-Pr$_2$W$_2$O$_9$. Thus, the dominating antiferromagnetic interaction at high-temperature changes to a weak ferromagnetic interaction at low-temperature. Over 30 K one can observe also 4-fold signal of hyperfine interaction type that disappears at about 50 K (Figs. 8c and 9). We suggest that the observed resonance line isn’t
attributed to the Pr$^{4+}$ ions but to tungstate W$^{5+}$ and W$^{4+}$ ones [12].

According to the crystal structure of typical double tungstates and molybdates, they nominally could consist of two kinds of paramagnetic centres: rare-earth RE$^{3+}$ ions with C$_2$ or lower point symmetry located at distorted dodecahedra and/or reduced transition metal Me$^{5+}$ ions located at octahedral sites. The tungsten or molybdate center is expected to undergo two subsequent one-electron reductions from Me$^{6+}$ to Me$^{4+}$. The intermediate Me$^{5+}$ is paramagnetic and shows a typical $S = 1/2$ signal with all g values usually below 2.0, which is still observable at temperatures as high as 100K [13]. In our samples there arise at least two non-equivalent positions of W$^{6+}$ (so also W$^{5+}$) ions that form chains of octahedral. The complex EPR spectrum we observed, consisting of at least two lines, suggests the presence of at least two types of paramagnetic entities, what clearly agree with a structure of the investigated samples. A change in the EPR line position suggests magnetic interaction between chains built of tungsten octahedra.

The EPR results for both praseodymium tungstates suggest that transition metal ions are well isolated each other in these types of structures, showing insignificant magnetic interaction.

3.4. XPS studies

II-Pr$_2$WO$_6$ and II-Pr$_2$W$_2$O$_9$ phases have also been analyzed by XPS method. The XPS Pr 3d lines for both compounds are shown in Fig. 10. The XP spectra are virtually identical for both samples. There are two distinct bands corresponding with the spin-orbit doublet Pr 3d$_{5/2}$ and Pr 3d$_{3/2}$. The maxima of Pr 3d$_{5/2}$ core level peaks were found to be at 933.1 $\pm$ 0.1 eV with the energy separation between Pr 3d$_{5/2}$ and Pr 3d$_{3/2}$ components being equal to 20.5 eV. The positions of the peaks are in good agreement with the literature values characteristic for praseodymium oxidation state Pr$^{3+}$ [14]. At the side of lower binding energies there is a well-defined shoulder ascribed to the shake-off satellite [15,16]. The presence of Pr$^{4+}$ oxidation state should produce the spectral line at 935.5 eV with the separation energy to Pr 3d$_{3/2}$ spin-orbit component equal to 17.8 eV[17]. With the lack of these components in the XPS Pr 3d spectrum there are no evidences on the existence of Pr$^{4+}$ oxidation state in the samples. However, considering relatively small sensitivity of XPS method, the presence of small quantities of Pr$^{4+}$ ions, probably mainly at the grain boundaries of both analyzed powdered samples, cannot be excluded.
dra [18,19]. The W 4f lines for all materials containing rare-earth ions are composed of two pairs of components. One of them can be definitely ascribed to W\(^{6+}\) oxidation states as in WO\(_3\) and their binding energies are 35.8 ± 0.1 eV. However, there is an additional component present in all rare-earth metal tungstates. Its maximum has been found at binding energy 34.7 ± 0.2 eV. This position is in the middle of the binding energies characteristic for W\(^{6+}\) (about 35.5 eV) and W\(^{4+}\) (about 32.5 eV) known from the literature [20]. The presence of an additional component in W 4f spectra of both investigated gadolinium tungstates (gadolinium can exist only in +3 oxidation state) puts in doubt the existence of W\(^{5+}\) oxidation state. It seems that the presence of low binding energy component in W 4f spectra of compounds under study is a reflection of prominent deformation of their crystal structure only at the surface of grains. The presence of vacancies in the anion sublattice due to an oxygen deficiency leads to the change of chemical state of tungsten ions and the presence of additional peak in XPS W 4f line. Very similar change of the XPS W 4f line shape was previously observed for nonstoichiometric WO\(_3\)\(_{x}\) oxides [18,21].

### Table 1

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4. Conclusions

Two praseodymium(III) tungstates II-Pr\(_2\)W\(_2\)O\(_9\) and II-Pr\(_2\)WO\(_6\) were synthesized by the high-temperature solid-state reaction between Pr\(_6\)O\(_{11}\) and WO\(_3\). On the basis of DTA studies it was confirmed the existence of only two Pr\(_2\)W\(_2\)O\(_9\) polymorphic modifications. Regardless of the type used gas for DTA–TG experiments, low-temperature polymorph of Pr\(_2\)W\(_2\)O\(_9\) undergoes reversible polymorphic transition practically at the same temperature, i.e. at about 1390 K. The I-Pr\(_2\)W\(_2\)O\(_9\) phase melts incongruently at about 1462 K both in the air and inert gas. Low-temperature form of Pr\(_2\)WO\(_6\) is thermally stable up to 1773 K. EPR results have shown a weak magnetic interaction between tungstate ions in both powder samples indicating on a good enough isolation between them in the structure. The resonance signal is coming mainly from W\(^{5+}\) (only hyperfine structure of the EPR spectra indicates on the presence of the W\(^{4+}\) ions) arising in the compounds due to two subsequent one-electron reductions from W\(^{6+}\) to W\(^{4+}\). XPS measurements confirm the conclusion. There have not been observed Pr\(^{4+}\) ions both in EPR and XPS experiments.

### References