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NEW PRASEODYMIUM(III) AND *d*-ELECTRON METALS TUNGSTATES OF THE FORMULA $MPr_2W_2O_{10}$ (*M*=Mn, Co, Cd)

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Three new compounds $MPr_2W_2O_{10}$ (*M*=Mn, Co, Cd) were prepared by the solid-state reaction. They are isostructural and crystallize in the orthorhombic system. $MPr_2W_2O_{10}$ (*M*=Mn or Co) melt incongruently above 1150°C and the solid product of melting is $Pr_2W_2O_9$. The $CdPr_2W_2O_9$ compound starts decomposing in the solid-state at 1156°C to $Pr_2W_2O_9$ and CdO.

Keywords: *DTA-TG, d-electron metal tungstates, IR, praseodymium(III) tungstate, XRD*

Introduction

Rare earth ions are characterised by incompletely filled the 4*f* orbitals. They can absorb an excitation energy to be at the excited state and then return to the ground state resulting in an emitting a radiation in the visible region. The *f–f* transitions in RE^{3+} ions have been found practical applications in laser host materials. As important optical materials, tungstates and molybdates of rare-earth metals have been used in quantum electronics [1], scintillators in medical devices and as phosphors (fluorescent lamps, X-ray detectors, cathode ray tubes) [2–5]. Inorganic pigments based on rare-earth compounds ($(Bi_2O_3)_{1-x}(Er_2O_3)_x$ [6], $(Bi_2O_3)_{1-x}(Ho_2O_3)_x$ [7]) are characterized by high covering and colouring power. They are materials, which are friendly for an environment and are often used in a production of paints, printing inks and plastics [6, 7].

In the present study, the new praseodymium(III) and *d*-electron metals tungstates with the formula $MPr_2W_2O_{10}$ (*M*=Mn, Co, Cd) have been prepared by the high-temperature solid-state reaction. This method of synthesis is often used to prepare phosphors, catalysts and other solid materials with interesting properties [8–10]. Thermal and some spectroscopic properties of $MPr_2W_2O_{10}$ have been investigated.

Experimental

Praseodymium(III) tungstate (Pr_2WO_6) and *d*-electron metal tungstates MWO_4 (*M*=Mn, Co and Cd) were used as the starting materials. Pr_2WO_6 was prepared using the solid-state reaction technique at high temperatures between Pr_6O_{11} (99.9%, Aldrich) and WO_3 (99.9%, Fluka). Divalent metal tungstates were obtained by a calcination in air the following mixtures: WO_3+$Mn(NO_3)_2{\cdot}4H_2O$ (99.9%, POCh), WO_3+$CoSO_4{\cdot}7H_2O$ (99.9%, Aldrich) and WO_3+$3CdSO_4{\cdot}8H_2O$ (99.99%, POCh). The mixtures of Pr_2WO_6 with MWO_4 were prepared with the following praseodymium(III) tungstate contents: 20.00; 25.00; 33.33; 45.00; 50.00; 55.00; 66.67; 75.00 and 90.00 mol%. The mixtures of Pr_2WO_6 with MWO_4 (*M*=Mn, Co) were heated in air, in 12 h periods at the following temperatures: 900, 950, 1000, 1025, 1050, 1075 and 1080°C. The $CdWO_4$+Pr_2WO_6 mixtures were calcinated in the following heating stages: 900°C (12 h); 950°C (12 h); 1000°C (12 h); 1025°C (12 h) and 1050°C (3·12 h). After each heating period the samples were gradually cooled to ambient temperature, weighed and grinded. No mass changes of samples were observed after each heating stage. A reaction progress was controlled on the base of the results of XRD analysis for the heated samples. After the final heating stage the samples were examined by DTA-TG and IR methods.

X-ray powder diffraction patterns of the analyzed samples were recorded on DRON-3 diffractometer using CuK_α radiation (λ=0.15418 nm). The scans were performed in the 2Θ range from 10 to 45° (step 0.02° and 1 s $step^{-1}$).

DTA-TG examinations were recorded with a Mettler Toledo TGA/SDTA 851 apparatus. These measurements were carried out within the temperature range 25–1400°C, in nitrogen (gas flow 15 mL min^{-1}), using corundum crucibles and at the heating rate of 10 K min^{-1}.

The IR spectra were recorded on a Specord M-80 spectrometer. The samples were pressed in pellets with KBr in the mass ratio of 1:100.

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Results and discussion

Reactivity in the solid-state between Pr_2WO_6 and MWO_4

The results of XRD analysis for the samples obtained after the final heating stage showed that the initial components are not mutually inert in air. Only one set of diffraction lines was identified on each powder diffraction pattern of samples obtained after heating equimolar MWO_4+Pr_2WO_6 mixtures. This set of reflexions cannot be considered to be characteristic for any of the used starting materials or other known praseodymium(III) tungstates (i.e., $Pr_2W_2O_9$, $Pr_6W_2O_{15}$, $Pr_8W_5O_{27}$, Pr_6WO_{12} and $Pr_2W_3O_{12}$ [11–18]) and neither for any known praseodymium oxides which form a homologous series with the general formula Pr_nO_{2n-2} (n=4, 5–6, 7, 8, 9, 10, 12, ∞) [19–25] nor any known M_xO_y (M=Mn, Co, Cd) [26–30]. XRD measurements of the samples, obtained by heating the mixtures comprising initially up to 50.00 mol% of Pr_2WO_6 showed the presence of two solid phases, i.e. MWO_4 and the new phases the diffraction lines sets of which were observed in diffractions patterns of samples comprising initially 50.00 mol% of Pr_2WO_6 and 50.00 mol% of MWO_4. In the concentration range above 50.00 mol% of Pr_2WO_6 it was found that two solid phases, i.e. Pr_2WO_6 and the new phases synthesized by heating equimolar mixtures Pr_2WO_6 with MWO_4, occurred in the samples on treatment.

On the base of the above information it can be stated that Pr_2WO_6 reacted with MWO_4 (M=Mn, Co and Cd) to the $MPr_2W_2O_{10}$ compounds. The reaction of Pr_2WO_6 with MWO_4 can be described by the following equation:

$$MnWO_{4(s)}+Pr_2WO_{6(s)}=MPr_2W_2O_{10(s)} \qquad (1)$$

Crystallography (from XRD data)

The powder diffraction patterns of samples obtained by calcination equimolar mixtures of MWO_4 with Pr_2WO_6 were subjected to indexing of the $MPr_2W_2O_{10}$ com-

Table 1 Results of indexing $MPr_2W_2O_{10}$ (M=Mn, Co, Cd) powder diffraction patterns

No.	$MnPr_2W_2O_{10}$			$CoPr_2W_2O_{10}$			$CdPr_2W_2O_{10}$			h	k	l
	d_{obs}/nm	d_{cal}/nm	100 I/I_0	d_{obs}/nm	d_{cal}/nm	100 I/I_0	d_{obs}/nm	d_{cal}/nm	100 I/I_0			
1	0.84090	0.84098	3	0.84011	0.84086	4	0.84090	0.84102	5	0	0	1
2	0.61636	0.61684	3	0.61551	0.61635	3	0.62109	0.62053	2	1	1	0
3	0.48531	0.48600	4	0.48531	0.48567	3	0.48610	0.48622	2	0	3	0
4	0.42827	0.42822	5	0.42786	0.42797	5	0.42950	0.42951	4	1	2	1
5	0.42045	0.42049	23	0.42045	0.42043	24	0.42065	0.42051	18	0	0	2
6	0.34743	0.34744	9	0.34729	0.34732	10	0.34823	0.34811	10	1	1	2
7	0.33143	0.33147	6	0.33119	0.33120	6	0.33362	0.33374	5	2	1	0
8	0.31788	0.31799	100	0.31788	0.31787	100	0.31821	0.31806	100	0	3	2
9	0.30841	0.30842	11	0.30820	0.30818	11	0.31020	0.31027	18	2	2	0
10	0.30010	0.30017	8	0.29991	0.29998	7	0.30069	0.30069	9	1	4	1
11	0.28956	0.28956	79	0.28938	0.28936	77	0.29113	0.29109	72	2	2	1
12	0.28036	0.28033	8	0.28036	0.28029	8	0.28053	0.28034	5	0	0	3
13	0.27607	0.27528	2				0.27533	0.27530	1	0	1	3
14	0.26788	0.26805	3	0.26788	0.26786	2	0.26843	0.26845	2	1	5	0
15	0.26040	0.26031	28	0.26018	0.26017	28	0.26151	0.26142	29	2	1	2
16	0.24873	0.24878	7	0.24853	0.24859	6	0.24980	0.24978	3	2	4	0
17	0.24410	0.24423	2	0.24410	0.24416	4	0.24423	0.24448	1	1	2	3
18	0.24289	0.24300	17	0.24276	0.24283	17	0.24314	0.24311	16	0	6	0
19	0.23854	0.23856	6	0.23842	0.23839	6	0.23946	0.23945	8	2	4	1
20	0.23336	0.23345	2	0.23330	0.23330	3				0	6	1
21	0.22605	0.22603	2	0.22594	0.22591	2				1	5	2
22	0.22147	0.22145	5	0.22132	0.22129	4	0.22226	0.22218	3	2	5	0
23	0.21419	0.21411	5	0.21400	0.21398	5	0.21482	0.21475	4	2	4	2
24	0.21132	0.21124	7	0.21118	0.21116	6	0.21165	0.21143	5	1	4	3
25	0.20754	0.20744	2	0.20736	0.20735	2	0.20818	0.20801	2	2	2	3
26	0.20570	0.20561	3	0.20548	0.20545	2	0.20686	0.20685	2	3	3	0

pounds. First successive diffraction lines recorded within 2Θ (CuK_α) 10–45° region were selected for indexing procedure performed by means of the POWDER program [31, 32]. Results of indexing the diffraction patterns of $MPr_2W_2O_{10}$ have been presented in Table 1. Table 2 shows the values of parameters of the unit cells as well as the values of experimental (obtained by degassing the samples and hydrostatic weighing in a pycnometric liquid – CCl_4) and calculated density for the new phases. The obtained phases are isostructural and crystallize in the orthorhombic system. On the base of a comparison of the powder diffraction patterns the author suggest that $MPr_2W_2O_{10}$ are not isostructural with the compounds characterized by an identical type of a chemical formula (i.e. $CoRE_2W_2O_{10}$ where *RE*=Y, Dy, Ho, Er [33] and $CuRE_2W_2O_{10}$ where *RE*=Nd, Sm, Eu, Gd [34, 35]).

Thermal properties

Figures 1 and 2 show DTA curves of $MPr_2W_2O_{10}$ (*M*=Mn or Co). On each DTA curve two endothermic effects were recorded up to 1400°C. No mass losses were recorded on the TG curves (not presented) up to the onsets of the first observed effects on the DTA curves. In order to determining melting behavior of the $MPr_2W_2O_{10}$ (*M*=Mn, Co) compounds additional experiments have made. Samples of these phases were heated in a furnace at the temperatures higher than the onsets of the first effects, i.e. at 1180°C (Mn); 1170°C (Co). After heating for 4 h the samples were quickly removed from a furnace and quenched to –10°C. On the base of observations of the residues obtained after heating it was found that both phases were melted. The results of XRD analysis made for the samples obtained this way showed that they contained $Pr_2W_2O_9$. Thus, the incongruent melting the $MPr_2W_2O_{10}$ compounds can be described by the following equation:

$$MPr_2W_2O_{10(s)} \rightarrow Pr_2W_2O_{9(s)} + \text{liquid} \qquad (2)$$

The endothermic effects with their onsets at 1225°C (Fig. 1, $MnPr_2W_2O_{10}$) and at 1228°C (Fig. 2, $CoPr_2W_2O_{10}$) are associated with melting $Pr_2W_2O_9$ [36–38]. Figure 3 shows DTA-TG curves of

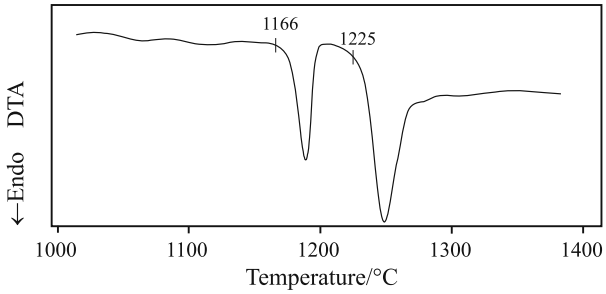

Fig. 1 DTA curve of $MnPr_2W_2O_{10}$

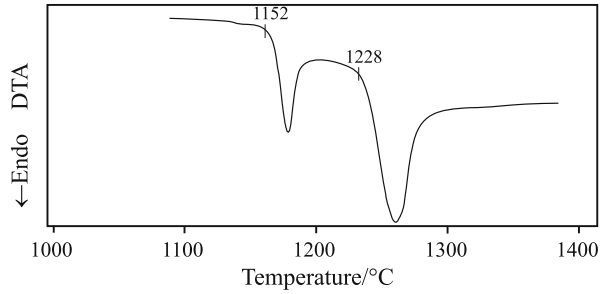

Fig. 2 DTA curve of $CoPr_2W_2O_{10}$

$CdPr_2W_2O_{10}$. Two endothermic effects with their onsets at: 1156 and 1221°C were recorded on the DTA curve of this compound. The first observed effect is accompanied by the mass loss (7.95 mass%, TG curve) starting at the same temperature. Consequently, samples of $CdPr_2W_2O_{10}$ were heated at the temperature higher than the onset of the first effect, i.e. 1180°C and then they were quickly removed from a furnace and next quenched to –10°C. The results of XRD measurements for the samples obtained this way showed that they contained $Pr_2W_2O_9$. It was also ascertained that the 'freezing' samples of $CdPr_2W_2O_{10}$ were not melted. Therefore, the decomposition of cadmium and praseodymium(III) tungstate in the solid-state can be described as the following process:

$$CdPr_2W_2O_{10(s)} = Pr_2W_2O_{9(s)} + CdO_{(g)} \qquad (3)$$

The calculated value of mass loss for the Eq. (3) equals 13.93 mass%. The experimental value is lower than the calculated one. It means that the decomposition process of $CdPr_2W_2O_{10}$ has not been finished under DTA-TG conditions. As in a case of the

Table 2 Calculated parameters of the $MPr_2W_2O_{10}$ unit cells and the values of experimental and calculated density

Compound (colour)	*a*/nm	*b*/nm	*c*/nm	ab^{-1}	cb^{-1}	V/nm^3	Z	ρ_{exp}/ g cm^{-3}	ρ_{cal}/ g cm^{-3}
$MnPr_2W_2O_{10}$ (brown)	0.68076(9)	1.4580(1)	0.84097(6)	0.4469	0.5768	0.83472(0)	4	6.82	6.88
$CoPr_2W_2O_{10}$ (green)	0.68021(5)	1.4570(1)	0.84086(3)	0.4669	0.5771	0.83335(6)	4	7.00	6.92
$CdPr_2W_2O_{10}$ (pistachio)	0.68567(2)	1.4586(7)	0.84102(4)	0.4701	0.5766	0.84116(8)	4	7.19	7.28

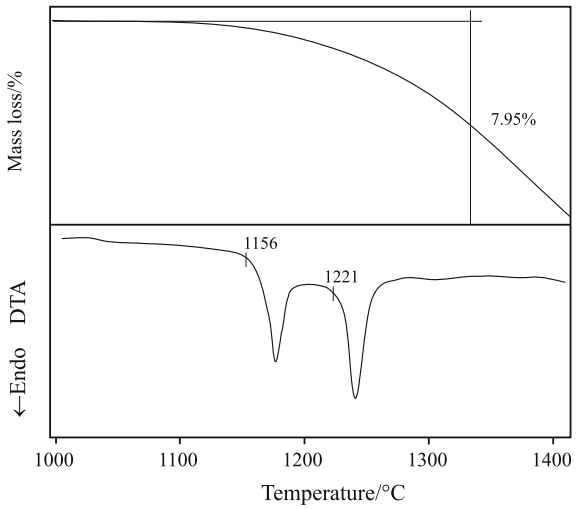

Fig. 3 TG-DTA curves of $CdPr_2W_2O_{10}$

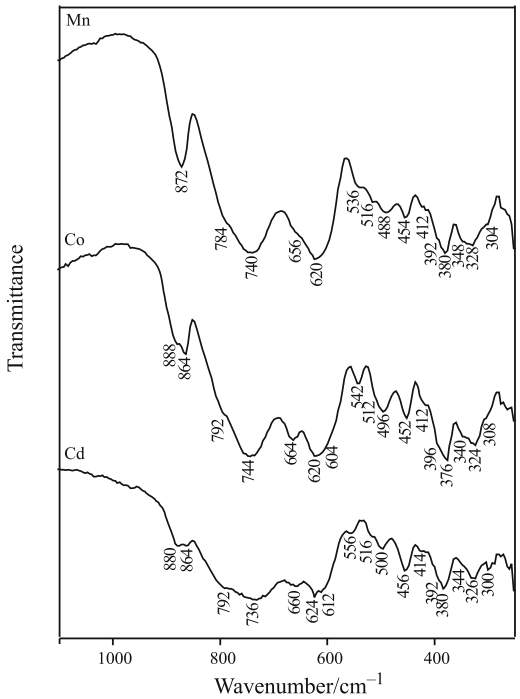

Fig. 4 IR spectra of $MPr_2W_2O_{10}$ compounds

$MPr_2W_2O_{10}$ compounds (*M*=Mn or Co), the endothermic effect with its onset at 1221°C is associated with melting $Pr_2W_2O_9$ [36–38].

Infrared spectra

As it is seen from Fig. 4, the spectra of $MPr_2W_2O_{10}$ show big similarity to each other. The absorption bands located at: 872 cm^{-1} (Mn); 884 and 864 cm^{-1} Co); 880 and 864 cm^{-1} (Cd) could be related to the stretching modes of the W–O bonds in joint WO_6 octahedra by oxygen bridges (three bridges per one octahedron) forming the structural elements $[(W_2O_9)^{6-}]^{\infty}$ [36, 39]. This structural element was found in structures of the $RE_2W_2O_9$ compounds (*RE*=Pr, Nd, Sm–Gd, the crystal structure of these compounds can be described by the following formula $RE^{[9]}RE^{[8]}(W_2^{[6]}O_9)^{\infty}$ [36, 39, 40]) and the stretching vibrations of the W–O bonds in the structural elements $[(W_2O_9)^{6-}]^{\infty}$ were observed in IR spectra of these compounds (the region of vibration frequencies 885–867 cm^{-1}) [39]. The several absorption bands in the frequencies region 792–604 cm^{-1} could be due to the asymmetric stretching vibrations of W–O bonds in joint WO_6 octahedra and also to the oxygen double bridge bonds WOOW [41–44]. According to the literature information [41–44] the absorption bands found in the IR spectra of all analyzed compounds below 556 cm^{-1} could be assigned to the symmetric and also asymmetric deformation modes of W–O bonds in joint WO_6 octahedra as well as to the deformation modes of the oxygen bridges WOOW.

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