Journal of Thermal Analysis and Calorimetry, Vol. 90 (2007) 1, 255–259

NEW COBALT AND RARE EARTH METAL TUNGSTATES $CoRE_2W_2O_{10}$
Their synthesis and some properties

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A new family of cobalt and rare-earth metal tungstates ($CoRE_2W_2O_{10}$ where *RE*=Y, Dy, Ho and Er) were synthesized by heating in the solid-state equimolar $CoWO_4$/RE_2WO_6 mixtures. The obtained compounds are isostructural and crystallize in the monoclinic system. They melt incongruently in an inert atmosphere at 1494 K ($CoY_2W_2O_{10}$), 1523 K ($CoDy_2W_2O_{10}$), 1517 K ($CoHo_2W_2O_{10}$) and 1493 K ($CoEr_2W_2O_{10}$). For each $CoRE_2W_2O_{10}$ compound the solid product of melting is an adequate RE_2WO_6.

Keywords: *cobalt tungstate, DTA-TG, IR, rare-earth metal tungstate*

Introduction

Chemistry of lanthanides has become of great importance over several decades because of its use in numerous applications [1–3]. Inorganic luminescent materials have found many practical applications in modern lighting and display fields, such as fluorescent lamps, catode-ray tubes, field emission displays and plasma display panels [4–9]. Our earlier studies on the reactivity in the solid-state between $ZnWO_4$ and RE_2WO_6 (*RE*=Y, Nd, Sm, Eu, Gd, Dy and Ho) showed that these compounds reacted to give family of isostructural compounds $ZnRE_4W_3O_{16}$ [10]. These compounds were synthesized by heating the appropriate $ZnWO_4$/RE_2WO_6 mixtures according to the following reaction [10]:

$$ZnWO_{4(s)}+2RE_2WO_{6(s)}=ZnRE_4W_3O_{16(s)} \qquad (1)$$

where $ZnRE_4W_3O_{16}$ crystallize in the orthorhombic system and melt incongruently or decompose in the solid-state above 1523 K [10]. In a solid-state as a result of the reaction between $CoWO_4$ and RE_2WO_6 (*RE*=Sm, Eu, Gd) two series of isostructural phases are formed: $Co_2RE_2W_3O_{14}$, $CoRE_4W_3O_{16}$ [11]. These phases were synthesized by means of a conventional ceramic method according to the following reactions:

$$CoWO_{4(s)}+2RE_2WO_{6(s)}=CoRE_4W_3O_{16(s)} \qquad (2)$$

$$2CoWO_{4(s)}+RE_2WO_{6(s)}=Co_2RE_2W_3O_{14(s)} \qquad (3)$$

where $Co_2RE_2W_3O_{14}$ crystallize in the orthorhombic system and melt congruently at ~1473 K [11]. The $CoRE_4W_3O_{16}$ phases also crystallize in the orthorhombic system and they are isostructural with the $ZnRE_4W_3O_{16}$ compounds. The $CoRE_4W_3O_{16}$ phases melt incongruently at ~1573 K [11]. This work presents the results of investigations concerning the reactivity in the solid-state between divalent metal tungstate with the wolframite structure ($CoWO_4$) and some rare-earth metal tungstates with the formula RE_2WO_6 (*RE*=Y, Dy, Ho and Er). Particular emphasis was laid on a determination of basic properties of the new obtained compounds $CoRE_2W_2O_{10}$.

Experimental

Materials

The starting materials were $CoWO_4$ and rare-earth metal tungstates (RE_2WO_6 where *RE*=Y, Dy, Ho, Er and Lu). Cobalt tungstate was synthesized by heating an equimolar mixture of $CoSO_4\cdot 7H_2O$ (99.998%, Aldrich) with WO_3 (99.9%, Fluka) at the following heating cycles: 873 K (12 h); 1073 K (12 h); 1173 K (12 h) and 1273 K (2·12 h). RE_2WO_6 were prepared by a solid-state reaction between an adequate rare-earth metal oxide RE_2O_3 (all oxides with a purity 99.9%, Aldrich) and WO_3 mixed at the molar ratio 1:1. The RE_2O_3/WO_3 mixtures were heated in air as described previously [10, 11].

The starting materials weighed in suitable molar proportion were ground manually in an agate mortar and heated in air, in the following cycles: 1173 K (1×12 h); 1273 K (1×12 h); 1323 K (1×12 h); 1373 K (1×12 h) and 1413 K (2×12 h). Additionally, the RE_2WO_6/$CoWO_4$ mixtures, where *RE*=Y, Ho, Er and Lu were heated at 1448 K (2×12 h). After each heating cycle the samples were gradually cooled down to room temperature, weighed, ground and analyzed using XRD method and afterwards heated until an equilibrium state had been established. After each heating cycle no mass changes of the mixtures were observed. After the final heating cycle the samples were examined by DTA-TG and IR methods.

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1388–6150/$20.00

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Methods

The DTA-TG examinations were performed using a Mettler Toledo TGA/SDTA851 apparatus. The experiments were carried out within the temperature range of 298–1773 K, in a nitrogen atmosphere, using corundum crucibles and the heating rate 10 K min^{-1}.

Routine phase analysis was made with a DRON-3 diffractometer at the CoK$_\alpha$ radiation (λ=0.179021 nm). Powder diffraction patterns were collected in the 2θ range 12–52° at the stepped scan rate of 0.02° per step and the count time of 1 s per step. For indexing purposes, diffraction patterns were made using an X'Pert PRO Philips diffractometer at the stepped scan rate of 0.02° per step and the count time of 10 s per step.

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

Results and discussion

Reaction of RE_2WO_6 (RE=Y, Dy, Ho, Er and Lu) with $CoWO_4$

The contents of initial $RE_2WO_6/CoWO_4$ (*RE*=Y, Dy, Ho, Er) mixtures and the results of XRD analysis of the carried out in an equilibrium state are presented in Table 1. The data in Table 1 indicate that the initial components of $RE_2WO_6/CoWO_4$ mixtures are not mutually inert in air. The XRD analysis of the samples, the initial mixtures of which contained up to 50 mol% of $CoWO_4$, showed that two solid phases were found in the treated samples, viz. the compounds: $CoWO_4$ and up to then unknown $CoRE_2W_2O_{10}$. At the molar ratio 1:1 of the $CoWO_4/RE_2WO_6$ mixtures, both reactants reacted completely to produce a series of new compounds:

$$CoWO_{4(s)}+RE_2WO_{6(s)}=CoRE_2W_2O_{10(s)} \quad (4)$$

On the other hand, the composition of the samples in an equilibrium, the initial mixtures of which contained over 50 mol% of RE_2WO_6, the compounds to remain in an equilibrium within the subsolidus area were $CoRE_2W_2O_{10}$ and RE_2WO_6 (Table 1). Moreover, it was found that the diffraction patterns of the samples obtained after the last heating cycle and initially comprising $Lu_2WO_6/CoWO_4$ contained only such diffraction lines that could be attributed to the starting materials.

Table 1 Contents of $RE_2WO_6/CoWO_4$ (*RE*=Y, Dy, Ho and Er) mixtures and results of XRD analysis of samples obtained after the final heating cycle

No.	RE_2WO_6 cotent in initial mixtures/mol%	Identified phases
1	10	$CoWO_4$, $CoRE_2W_2O_{10}$
2	20	$CoWO_4$, $CoRE_2W_2O_{10}$
3	25	$CoWO_4$, $CoRE_2W_2O_{10}$
4	30	$CoWO_4$, $CoRE_2W_2O_{10}$
5	33.33	$CoWO_4$, $CoRE_2W_2O_{10}$
6	40	$CoRE_2W_2O_{10}$, $CoWO_4$
7	50	$CoRE_2W_2O_{10}$
8	60	$CoRE_2W_2O_{10}$, RE_2WO_6
9	66.67	$CoRE_2W_2O_{10}$, RE_2WO_6
10	75	RE_2WO_6, $CoRE_2W_2O_{10}$
11	80	RE_2WO_6, $CoRE_2W_2O_{10}$
12	90	RE_2WO_6, $CoRE_2W_2O_{10}$

Characteristic of $CoRE_2W_2O_{10}$ compounds

Crystallography from XRD data

The powder diffraction patterns of the samples in an equilibrium state initially comprising $CoWO_4$ and RE_2WO_6 mixed at the molar ratio of 1:1 were subjected to indexing the $CoRE_2W_2O_{10}$ compounds. The diffraction lines recorded within 2θ (CoK$_{\alpha aver}$) 12–48° region were selected for indexing by Powder [12, 13] and Dicvol [14, 15] programs. Very similar values of the unit cells of the $CoRE_2W_2O_{10}$ phases were obtained during indexing procedure by these programs [12–15]. Table 2 shows the results of indexing the $CoRE_2W_2O_{10}$ powder diffraction patterns. The parameters of $CoRE_2W_2O_{10}$ unit cells, the values of experimental (obtained by degassing samples and hydrostatic weighing in pycnometric liquid – CCl_4) and theoretical densities were tabulated in Table 3.

DTA-TG studies

Figure 1 shows the DTA curves of the $CoRE_2W_2O_{10}$ compounds. On each DTA curves only one endothermic effect was recorded up to 1773 K. No mass losses were recorded on the TG curves (not presented) up to the onsets of the observed endothermic effects on the DTA curves. On the base of the DTA-TG results and observations of the residues in crucibles obtained after DTA-TG studies it was found that the effects with their onsets at: 1494 K (Y), 1523 K (Dy), 1517 K (Ho) and 1493 K (Er) are associated with melting the $CoRE_2W_2O_{10}$ phases. On the base of the XRD method it was found that $CoRE_2W_2O_{10}$ samples heated in a furnace for 2 h above their melting points, i.e. at 1513 K (Y), 1538 K (Dy), 1533 K (Ho), 1513 K or (Er) and then quickly quenched to 263 K contained the corresponding RE_2WO_6. Thus, the incongruent melting $CoRE_2W_2O_{10}$ can be described by the following equation:

$$CoRE_2W_2O_{10(s)}\rightarrow RE_2WO_{6(s)}+\text{liquid} \quad (5)$$

Table 2 Results of indexing $CoRE_2W_2O_{10}$ powder diffraction patterns

No.	$CoY_2W_2O_{10}$		$CoDy_2W_2O_{10}$		$CoHo_2W_2O_{10}$		$CoEr_2W_2O_{10}$		*h k l*
	d_{obs}/nm	I/I_0/%	d_{obs}/nm	I/I_0/%	d_{obs}/nm	I/I_0/%	d_{obs}/nm	I/I_0/%	
1	0.76655	8	0.76940	12	0.76769	8	0.76598	10	0 1 0
2			0.65323	2	0.65240	4	0.65117	4	0 0 2
3	0.55769	4	0.55979	5	0.55799	8	0.55709	6	2 0 0
4	0.47374	12	0.47568	8	0.47417	6	0.47352	6	1 1 $\bar{2}$
5	0.44472	3	0.44548	4	0.44491	6	0.44416	4	2 1 $\bar{1}$
6	0.43440	3	0.43730	3	0.43548	4	0.43512	4	1 1 2
7	0.40964	14	0.41141	13	0.41076	12	0.41028	12	2 1 1
8	0.38479	6	0.38507	7	0.38535	6	0.38507	6	0 2 0
9	0.36751	8	0.36905	11	0.36815	11	0.36777	10	0 2 1
10			0.34991	4	0.34910	4	0.34899	2	3 0 $\bar{2}$
11			0.34356	3	0.34202	4	0.34180	4	3 0 1
12	0.33054	10	0.33126	14	0.33085	12	0.33034	12	0 2 2
13	0.32719	16	0.32800	21	0.32749	20	0.32709	18	1 0 $\bar{4}$
14	0.30386	90	0.30525	87	0.30455	92	0.30438	90	2 0 $\bar{4}$
15	0.30190	30	0.30301	26	0.30249	34	0.30232	25	3 0 2
16	0.29896	6	0.30021	8	0.29971	6	0.29946	6	1 0 4
17	0.29559	100	0.29681	100	0.29624	100	0.29600	100	2 2 $\bar{2}$
18	0.29286	4	0.29381	6	0.29317	6	0.29293	4	2 1 3
19	0.27879	30	0.28023	32	0.27951	31	0.27937	30	4 0 0
20							0.27269	6	4 0 $\bar{2}$
21	0.26694	4	0.26792	2	0.26713	6	0.26700	4	3 2 0
22	0.26206	16	0.26294	21	0.26225	24	0.26206	18	4 1 0
23	0.25743	6	0.25803	2		1			4 1 $\bar{2}$
24	0.25297	4	0.25390	2					3 1 $\bar{4}$
25	0.25129	8	0.25175	4	0.25157	4	0.25140	6	0 3 1
26	0.24496	6	0.24694	8			0.24534	6	0 1 5
27	0.24464	8	0.24562	9	0.24551	9	0.24496	8	2 2 3
28	0.24184	50	0.24275	46	0.24238	40	0.24222	40	4 0 2
29	0.23738	8	0.23810	8					3 2 2
30	0.22977	2	0.23039	2	0.23000	2	0.22986	2	1 3 2
31			0.22454	2					2 3 $\bar{2}$
32	0.22262	2	0.22324	2	0.22289	2	0.22280	2	4 2 $\bar{2}$
33	0.21816	6	0.21919	8	0.21850	8	0.21842	4	4 0 3

Table 3 Calculated parameters of unit cells for $CoRE_2W_2O_{10}$ (Z=6) and values of experimental and theoretical densities

	a/nm	*b*/nm	*c*/nm	β/°	Experimental density/kg m^{-3}	Theoretical density/kg m^{-3}
$CoY_2W_2O_{10}$	1.1311(8)	0.76678(3)	1.3191(6)	99.584(7)	6730	6770
$CoDy_2W_2O_{10}$	1.1360(5)	0.76969(8)	1.3235(2)	99.651(7)	7940	7960
$CoHo_2W_2O_{10}$	1.1332(6)	0.76755(2)	1.3213(4)	99.602(8)	8040	8060
$CoEr_2W_2O_{10}$	1.1296(6)	0.76713(2)	1.3211(4)	99.527(5)	8070	8130

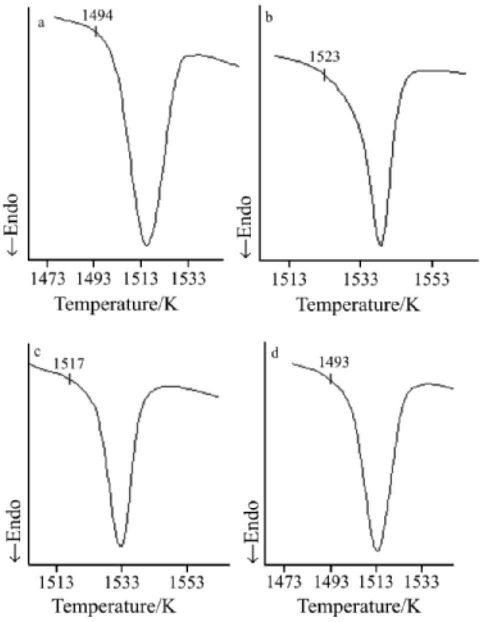

Fig. 1 DTA curves of $CoRE_2W_2O_{10}$ compounds: a – $CoY_2W_2O_{10}$, b – $CoDy_2W_2O_{10}$, c – $CoHo_2W_2O_{10}$ and d – $CoEr_2W_2O_{10}$

IR spectra

Figure 2 shows IR spectra of the $CoRE_2W_2O_{10}$ compounds. As it can be seen from the figure, the IR spectra of these compounds show a big similarity one to the other. In the light of literature information concerning binary and ternary lanthanide tungstates with octahedric coordination of W ions by oxygen ions [16–21], the absorption bands with their maxima at ~870 cm^{-1} can be assigned to the symmetric stretching modes of W–O bonds in joint WO_6 octahedra forming structure elements $(W_2O_9)^{6-}$ (three oxygen bridges per octahedron). The several absorption bands in the 770–500 cm^{-1} region can 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 [16–21]. The oxygen bridge bonds are present in the anion lattice of many binary and ternary rare-earth tungstates [16–21]. The absorption bands found in the IR spectra of the $CoRE_2W_2O_{10}$ compounds below 500 cm^{-1} can be due 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 [16–21].

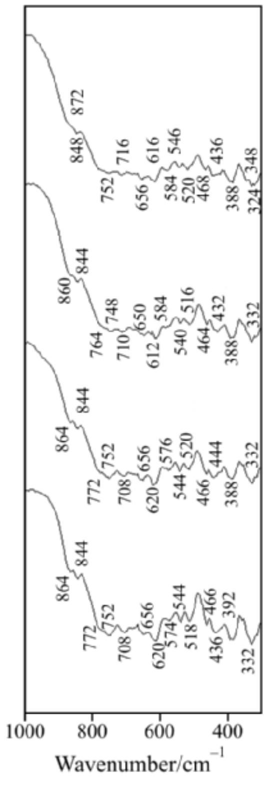

Fig. 2 IR spectra of $CoRE_2W_2O_{10}$

Conclusions

The obtained experimental results lead to the following conclusions:

- a new series of cobalt and rare-earth metal tungstates $CoRE_2W_2O_{10}$ (*RE*=Y, Dy, Ho and Er) was synthesized the solid-state reaction between $CoWO_4$ and RE_2WO_6 mixed at the molar ratio of 1:1
- Lu_2WO_6 does not enter into a reaction with $CoWO_4$
- the $CoRE_2W_2O_{10}$ compounds are isostructural and crystallize in the monoclinic system
- the lattice parameters and cell volumina of the $CoRE_2W_2O_{10}$ phases decrease with decreasing radius of the rare-earth ion
- the $CoRE_2W_2O_{10}$ compounds melt congruently at ~1500 K in an inert atmosphere, the solid product of melting is an adequate RE_2WO_6
- the melting point of the $CoRE_2W_2O_{10}$ compounds slightly decreases from Dy to Er
- $CoRE_2W_2O_{10}$ melt slightly higher than the $Co_2RE_2W_3O_{14}$ compounds (*RE*=Sm, Eu, Gd, melting points ~1473 K) [11]
- $CoRE_2W_2O_{10}$ are less stable thermally than the $CoRE_4W_3O_{16}$ compounds (*RE*=Sm, Eu, Gd, melting points ~1573 K) [11]
- the anion lattice of new cobalt and rare-earth metal tungstates is built by the joint WO_6 octahedra forming $(W_2O_9)^{6-}$ groups

References

1 P. Sulcova and M. Trojan, J. Therm. Anal. Cal., 83 (2006) 557.
2 K. Akiyama, H. Aoyama, N. Abe, T. Tojo, H. Kawaji and T. Atake, J. Therm. Anal. Cal., 81 (2005) 583.

3 P. Sulcova, J. Therm. Anal. Cal., 82 (2005) 51.
4 G. Blasse and B. C. Grabmaier, Luminescent Materials, Springer, Berlin, Heidelberg 1994.
5 C. Feldmann, T. Jüstel, C. R. Ronda and P. J. Schmidt, Adv. Funct. Mater., 13 (2003) 511.
6 Y. Zhou and J. Lin, J. Solid State Chem., 178 (2005) 441.
7 P. Zhang, Z. Hong, M. Wang, X. Fang, G. Qian and Z. Wang, J. Lumin., 113 (2005) 89.
8 R. Scheps, Prog. Quant. Electron, 20 (1996) 271.
9 E. Downing, L. Hesselink, J. Raltson and R. Macfarlane, Science, 273 (1996) 1185.
10 E. Tomaszewicz, Solid State Sci., 8 (2006) 508.
11 E. Tomaszewicz, Thermochim. Acta, 447 (2006) 69.
12 D. Taupin, J. Appl. Cryst., 1 (1968) 78.
13 D. Taupin, J. Appl. Cryst., 6 (1973) 380.
14 D. Louer and M. Louer, J. Appl. Cryst., 5 (1972) 271.
15 A. Boultif and D. Louer, J. Appl. Cryst., 24 (1991) 987.
16 V. I. Tsaryuk and V. F. Zolin, Spectrochim. Acta, A57 (2001) 355.
17 J. Hanuza, M. Mączka and J. H. van der Maas, J. Solid State Chem., 117 (1995) 177.
18 M. Daturi, G. Busca, M. M. Borel, A. Leclaire and P. Piaggio, J. Phys. Chem., B101 (1997) 4358.
19 J. Hauck and A. Fadini, Z. Naturforsch., B25 (1970) 422.
20 M. Mączka, J. Solid State Chem., 129 (1997) 287.
21 J. Hanuza, L. Macalik, M. Mączka, E. T. G. Lutz and J. H. van der Maas, J. Mol. Struct., 511–512 (1999) 85.

Received: June 2, 2006
Accepted: August 23, 2006
OnlineFirst: February 13, 2007

DOI: 10.1007/s10973-006-7721-0