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Reactivity in the solid state between $CoWO_4$ and RE_2WO_6 where RE = Sm, Eu, Gd

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Abstract

Reactivity in the solid state between $CoWO_4$ and some rare-earth metal tungstates RE_2WO_6 (RE = Sm, Eu, Gd) was investigated by the XRD method. Two families of new isostructural cobalt and rare-earth metal tungstates, $Co_2RE_2W_3O_{14}$ and $CoRE_4W_3O_{16}$, were synthesized. The $Co_2RE_2W_3O_{14}$ phases are formed by heating in air the $CoWO_4$ and RE_2WO_6 compounds mixed at the molar ratio 2:1, while the $CoRE_4W_3O_{16}$ phases are synthesized at the molar ratio of $CoWO_4/RE_2WO_6$ equals to 1:2. The $Co_2RE_2W_3O_{14}$ phases as well as the $CoRE_4W_3O_{16}$ compounds crystallize in the orthorhombic system. The $Co_2RE_2W_3O_{14}$ and $CoRE_4W_3O_{16}$ compound melt above 1150 °C. A melting manner of the $Co_2RE_2W_3O_{14}$ and $CoRE_4W_3O_{16}$ compounds was determined in an inert atmosphere. The formation of $CoWO_{4-x}$ phase was observed during heating in an inert atmosphere.

Keywords: Rare-earth metal tungstates; Cobalt tungstate; Reactivity in the solid state

1. Introduction

During the past decade oxide-based inorganic phosphors have been extensively investigated for their optical applications [1,2]. Phosphors play an important role in high-resolution devices such as cathode-ray tubes, electroluminescent devices, plasma display panels and field emission displays [3–6].

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 the family of isostructural compounds $ZnRE_4W_3O_{16}$ [7]. As it was found $ZnRE_4W_3O_{16}$ were synthesized by heating in air appropriate $ZnWO_4/RE_2WO_6$ mixtures according to the following reaction [7]:

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

The family of compounds $ZnRE_4W_3O_{16}$ crystallize in the orthorhombic system. These compounds melt incongruently or decompose in the solid state above 1250 °C. The photoluminescence spectra of the $ZnEu_4W_3O_{16}$ compound were measured in the 250–600 nm under excitation at 613 nm. These experiments prove that the $ZnEu_4W_3O_{16}$ compound is shown to be potentially attractive as photoluminophor.

This work presents the results of investigations concerning the reactivity between other divalent metal tugnstate with the wolframite structure ($CoWO_4$) with some rare-earth metal tungstates RE_2WO_6 (RE = Sm, Eu, Gd).

2. Experimental details

2.1. Sample preparation

The starting materials were $CoWO_4$ and rare-earth metal tungstates with the formula RE_2WO_6 (RE = Sm, Eu, Gd). For experiments $CoWO_4$ was prepared by two independent methods. Cobalt tungstate was obtained by precipitation from aqueous solution [8]. In order to synthesize $CoWO_4$ by this method stoichiometric amount of analytical grade $CoSO_4 \cdot 7H_2O$ and $Na_2WO_4 \cdot 2H_2O$ were dissolved in double-distilled water. The solution of the cobalt salt was brought to a boil and to then, a hot solution comprising Na_2WO_4 was added. The obtained precipitate was washed, dried, ground and annealed in a furnace at 800 °C (12 h) and 1000 °C (12 h). Cobalt tungstate was synthesized by conventional ceramic method, too. An equimo-

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lar mixture of $CoSO_4{\cdot}7H_2O$ with WO_3 was heated in air at the following heating cycles: 600 °C (12 h); 800 °C (12 h); 900 °C (12 h) and 1000 °C (2 × 12 h). A characterization using the X-ray powder diffraction method showed that the obtained by both methods powders were indeed $CoWO_4$ and revealed no presence of any chemical impurities. The disadvantage of "wet" method is problem with removing adsorbed by obtained precipitate Na^+ and SO_4^{2-} ions (necessity of repeated washing precipitate). The disadvantage of ceramic method is SO_2 evaluated in significant amounts.

RE_2WO_6 were synthesized by the solid state reaction between RE_2O_3 (Sm_2O_3-mixture of cubic and monoclinic modifications, Eu_2O_3-cubic, Gd_2O_3-cubic) and WO_3 mixed at the molar ratio 1:1. The RE_2O_3/WO_3 mixtures were heated in the following cycles: 800 °C (12 h), 900 °C (12 h), 1000 °C (12 h) and 1100 °C (2 × 12 h).

The starting materials, i.e. RE_2WO_6 and $CoWO_4$, weighed in suitable molar proportion, were ground and heated in air in the following heating cycles: 1000 °C (12 h); 1050 °C (12 h); 1075 °C (12 h); 1100 °C (12 h); 1125 °C (12 h); 1150 °C (12 h). After each heating cycle, the samples were cooled gradually to ambient temperature, weighed, ground and analyzed by the XRD method and afterwards heated until an equilibrium state had been established. After the final heating cycle all samples were examined by DTA/TG and IR methods.

2.2. *Characterization methods*

Routine phase analysis was conducted with a DRON-3 diffractometer using the Co Kα radiation ($\lambda = 1.79021$ Å). Diffraction patterns were collected over 12–60° 2Θ at the stepped scan rate of 0.02° per step and the count time of 1 s per step. For indexing procedure, powder diffraction patterns were collected 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 DTA-TG examinations were performed using a Mettler Toledo TGA/SDTA851 apparatus. These measurements were carried out within the temperature range of 20–1500 °C, in a nitrogen atmosphere, using corundum crucibles and at the heating rate of 10 K min^{-1}.

The IR spectra were recorded on a Specord M-80 spectrometer (Carl Zeiss Jena). For the sample preparation, the technique of KBr pellet was used.

3. Results and discussion

3.1. *Reaction of RE_2WO_6 (RE = Sm, Eu, Gd) with $CoWO_4$*

Table 1
The molar ratio $RE_2WO_6/CoWO_4$ (RE = Sm, Eu, Gd) in initial mixtures and the phases identified by XRD analysis of the samples at room temperature

No.	RE_2WO_6 content in initial mixtures (mol%)	Identified phases
1	10	$CoWO_4$, $Co_2RE_2W_3O_{14}$
2	25	$Co_2RE_2W_3O_{14}$, $CoWO_4$
3	33.33	$Co_2RE_2W_3O_{14}$
4	40	$Co_2RE_2W_3O_{14}$, $CoRE_4W_3O_{16}$
3	50	$Co_2RE_2W_3O_{14}$, $CoRE_4W_3O_{16}$
5	60	$Co_2RE_2W_3O_{14}$, $CoRE_4W_3O_{16}$
6	65	$CoRE_4W_3O_{16}$, $Co_2RE_2W_3O_{16(traces)}$
7	66.67	$CoRE_4W_3O_{16}$
8	70	$CoRE_4W_3O_{16}$, RE_2WO_6
9	75	$CoRE_4W_3O_{16}$, RE_2WO_6
10	90	RE_2WO_6, $CoRE_4W_3O_{16}$

Table 1 shows the contents of initial mixtures and the XRD analysis results of samples obtained after the last heating $CoWO_4/RE_2WO_6$ (RE = Sm, Eu, Gd) mixtures. The data of Table 1 point out that $CoWO_4$ excess does not appear if RE_2WO_6mole percent exceeds 33.33%. These compounds enter into reaction to give two series of new compounds: $Co_2RE_2W_3O_{14}$ and $CoRE_4W_3O_{16}$. XRD analysis made for the samples, the initial mixtures of which contained to 33.33 mol% of RE_2WO_6, showed that two solid phases were occurring in the samples on treatment, viz. the compounds: $CoWO_4$ and $Co_2RE_2W_3O_{14}$. Thus, the compositions of the samples examined imply that within the component concentration range to 33.33 mol% of RE_2WO_6, the rare-earth metal tungstate reacts completely with $CoWO_4$ to give $Co_2RE_2W_3O_{14}$:

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

At this concentration range, due to a full involvement of RE_2WO_6 in to the reaction (2), $CoWO_4$ occurs in excess and remains as a separate phase in equilibrium with $Co_2RE_2W_3O_{14}$. At the molar ratio 2:1 of the $CoWO_4/RE_2WO_6$ mixtures, both reactants react to completion. On the other hand, the composition of samples at equilibrium, the initial mixtures of which contained over 33.33 mol% of RE_2WO_6, shows that in the RE_2WO_6–$CoWO_4$ systems, apart from $Co_2RE_2W_3O_{14}$ other series of compounds—$CoRE_4W_3O_{16}$, is formed. The presence of $CoRE_4W_3O_{16}$ in those samples proves that other reactions run there, too:

$$CoWO_{4(s)} + 2RE_2WO_{6(s)} = CoRE_4W_3O_{16(s)} \quad (3)$$

The run of reactions (3) implies that the compounds $Co_2RE_2W_3O_{14}$ and $CoRE_4W_3O_{16}$ were in equilibrium in the concentration range of 33.33–66.67 mol% of RE_2WO_6. The composition of samples obtained after heating the initial mixtures composed of 33.33 mol% of $CoWO_4$ and 66.67 mol% of RE_2WO_6 confirms the quantitative course of the reactions (3). In the other concentration range, i.e. over 66.67 mol% of RE_2WO_6, the compounds to remain at equilibrium within the subsolidus area will be $CoRE_4W_3O_{16}$ and RE_2WO_6 (Table 1). Additionally, two independent mixtures of which containing 25 mol% of $CoRE_4W_3O_{16}$ and 75 mol% of $CoWO_4$ as well as 25 mol% of $Co_2RE_2W_3O_{16}$ and 75 mol% of RE_2WO_6 were prepared. These mixtures were heated under the same conditions as those applied to the preparation of samples obtained from $CoWO_4/RE_2WO_6$ mixtures. XRD analysis made for the samples containing initially $CoWO_4/CoRE_4W_3O_{16}$ and $RE_2WO_6/Co_2RE_2W_3O_{16}$ showed that in the $CoWO_4$-RE_2WO_6 (RE = Sm, Eu, Gd) sys-

Table 2
Calculated parameters of the unit cells for $Co_2RE_2W_3O_{14}$ ($Z = 6$) and values of their experimental and theoretical densities

	a (Å)	*b* (Å)	*c* (Å)	Experimental density (g/cm^3)	Theoretical density (g/cm^3)
$Co_2Sm_2W_3O_{14}$	6.7776(5)	15.529(1)	14.910(4)	7.56	7.58
$Co_2Eu_2W_3O_{14}$	6.7558(5)	15.438(0)	14.883(7)	7.66	7.68
$Co_2Gd_2W_3O_{14}$	6.7521(8)	15.355(8)	14.790(8)	7.81	7.84

Table 3
Calculated parameters of the unit cells for $CoRE_4W_3O_{16}$ ($Z = 3$) and values of their experimental and theoretical densities

	a (Å)	*b* (Å)	*c* (Å)	Experimental density (g/cm^3)	Theoretical density (g/cm^3)
$CoSm_4W_3O_{16}$	17.6494(5)	7.3921(2)	7.2990(6)	7.63	7.68
$CoEu_4W_3O_{16}$	17.5799(2)	7.3728(2)	7.2848(0)	7.72	7.78
$CoGd_4W_3O_{16}$	17.5439(8)	7.3496(3)	7.2658(4)	7.90	7.95

tems other reactions run, too:

$$CoRE_4W_3O_{16(s)} + 3CoWO_{4(s)} = 2Co_2RE_2W_3O_{14(s)} \quad (4)$$

$$Co_2RE_2W_3O_{14(s)} + 3RE_2WO_{6(s)} = 2CoRE_4W_3O_{16(s)} \quad (5)$$

3.2. *Characteristic of $Co_2RE_2W_3O_{14}$ and $CoRE_4W_3O_{16}$ compounds*

3.2.1. *Crystallography (from XRD data)*

Powder diffraction patterns of samples in an equilibrium state comprising initially 33.33 and 66.67 mol% RE_2WO_6 were subjected to indexing the $Co_2RE_2W_3O_{14}$ and $CoRE_4W_3O_{16}$ phases, respectively. Diffraction lines recorded within 2Θ (Co K$\alpha_{average}$) 12–47° (for $Co_2RE_2W_3O_{14}$) and 12–60° (for $CoRE_4W_3O_{16}$) region were selected for indexing by POWDER [9,10] and DICVOL [11,12] programs. Very similar values of the unit cells for $Co_2RE_2W_3O_{14}$ and the unit cells for $CoRE_4W_3O_{16}$ were obtained during indexing procedure by these programs. Supplementary Tables S1 and S2 show the results of indexing the powder diffraction patterns of $Co_2RE_2W_3O_{14}$ and $CoRE_4W_3O_{16}$, respectively. The parameters of $Co_2RE_2W_3O_{14}$ and $CoRE_4W_3O_{16}$ unit cells and the values of experimental (obtained by degassing samples and hydrostatic weighing in pycnometric liquid—CCl_4) and theoretical density have been tabulated in Tables 2 and 3, respectively. The data of Supplementary Table S1 and Table 2 show that the $Co_2RE_2W_3O_{14}$ compounds are isostructrural and the lattice parameters and cell volumina of theses phases decrease with decreasing of the rare-earth ion radius. The data of Supplementary Table S2 and Table 3 point out that the $CoRE_4W_3O_{16}$ phases form a family of isostructural compounds. Fig. 1 shows the powder diffraction patterns of two phases from among the $ZnRE_4W_3O_{16}$ and $CoRE_4W_3O_{16}$ families. Fig. 1 confirms that the $CoRE_4W_3O_{16}$ compounds are isostructural with the $ZnRE_4W_3O_{16}$ phases. Analogously to the case of the $Co_2RE_2W_3O_{14}$ compounds, the lattice parameters and cell volumina of the $CoRE_4W_3O_{16}$ phases decrease from Sm to Gd.

3.2.2. *Thermal properties*

DTA-TG examinations were performed in an inert atmosphere (N_2) for the RE_2WO_6, $CoWO_4$, $Co_2RE_2W_3O_{14}$ and $CoRE_4W_3O_{16}$ compounds. The DTA curves of RE_2WO_6 do not evidence any thermal effects up to 1500 °C. Fig. 2 shows DTA-TG curves of $CoWO_4$. A very small mass loss (~0.09% by weight) was recorded on the TG curve of $CoWO_4$ at ~900 °C. During heating a sample of $CoWO_4$ with the heating rate 10 K min^{-1} no effect was recorded on the DTA curve of this compound at ~900 °C (Fig. 2). Thus, separate samples of $CoWO_4$ were heated: at 900 °C in nitrogen atmosphere (for 2 h) as well as at 900 and 1000 °C in air (for 2 h). After heating, the samples were cooled to ambient temperature and examined by the XRD method. On the base of the XRD analysis it was found that positions of all diffraction lines recorded in the diffraction

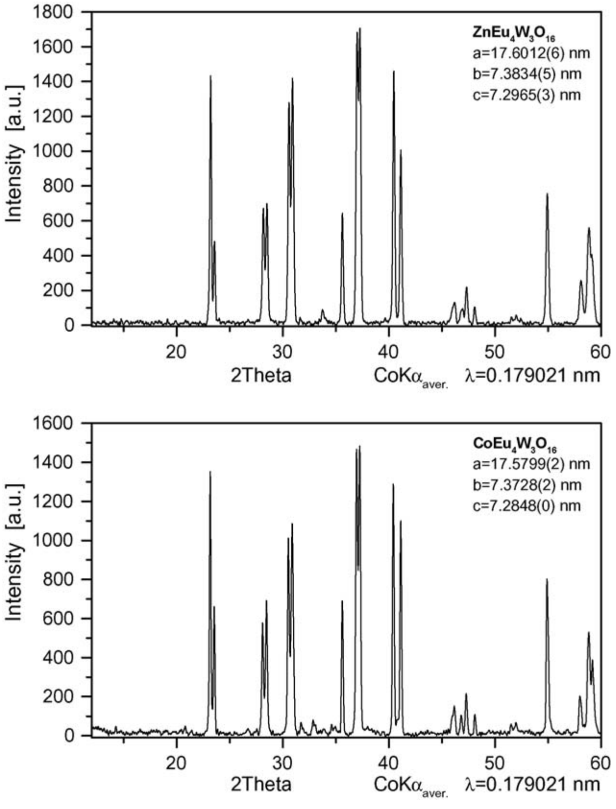

Fig. 1. Powder diffraction patterns of $ZnEu_4W_3O_{16}$ and $CoEu_4W_3O_{16}$ compounds.

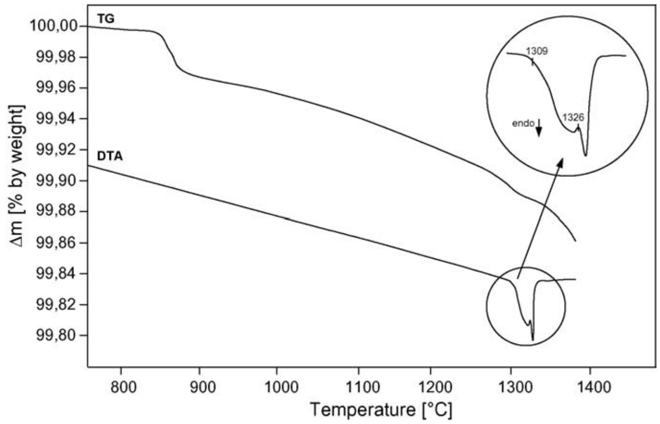

Fig. 2. DTA-TG curves of $CoWO_4$ (an inert atmosphere; heating rate, $10\,K\,min^{-1}$).

pattern of $CoWO_4$ heated in an inert atmosphere are identical in comparison to positions of the diffraction lines recorded in the diffraction pattern of $CoWO_4$ used for experiments. However, an appearance of one additional diffraction line ($d = 2.1322$ Å, relative intensity $I = 2\%$) was observed in the powder diffraction pattern of $CoWO_4$ heated in nitrogen. This diffraction line was not observed of the diffraction patterns of $CoWO_4$ heated in air. On the base of the conducted experiments the author suggests that in an inert atmosphere and at ∼900 °C $CoWO_4$ undergoes a decomposition. This process is connected with a liberation of a small amount of oxygen and a formation of hitherto unknown $CoWO_{4-x}$. The endothermic effects recorded on the DTA curve of $CoWO_4$ with their onsets at 1309 and 1326 °C are probably associated with incongruent melting $CoWO_{4-x}$. On the DTA-TG curves (not presented) of $CoWO_4$ recorded up to 1000 °C in air no effects and mass losses were recorded. For technical reasons (a very fast wearing off of a heating element during experiments conducted in air and the temperatures above 1000 °C) DTA-TG measurements in air were conducted only up to 1000 °C.

Fig. 3 shows the DTA curves of the $Co_2RE_2W_3O_{14}$ compounds. On each DTA curve of these compounds only one endothermic effect was recorded up to 1500 °C. On the base of the DTA-TG results and observations of the residue obtained after the DTA-TG examinations it was found that the effects with their onsets at: 1170 °C (Sm), 1187 °C (Eu) and 1209 °C (Gd) are associated with melting $Co_2RE_2W_3O_{14}$. On the base of the XRD method it was found that the $Co_2RE_2W_3O_{14}$ samples heated above their melting points, i.e. at 1190 °C (Sm), 1205 °C (Eu), 1225 °C (Gd) and then quickly quenched contained one solid phase $Co_2RE_2W_3O_{14}$. Fig. 4 shows DTA curves of the $CoRE_4W_3O_{16}$ compounds. Only one endothermic effect was recorded on each of DTA curves of the $CoRE_4W_3O_{16}$ phases. The endothermic effects with their onsets at: 1292 °C (Sm), 1296 °C (Eu) and 1303 °C (Gd) are associated with melting the $CoRE_4W_3O_{16}$ phases. This fact may be confirmed by our observations of the residue in a crucible obtained after the DTA-TG

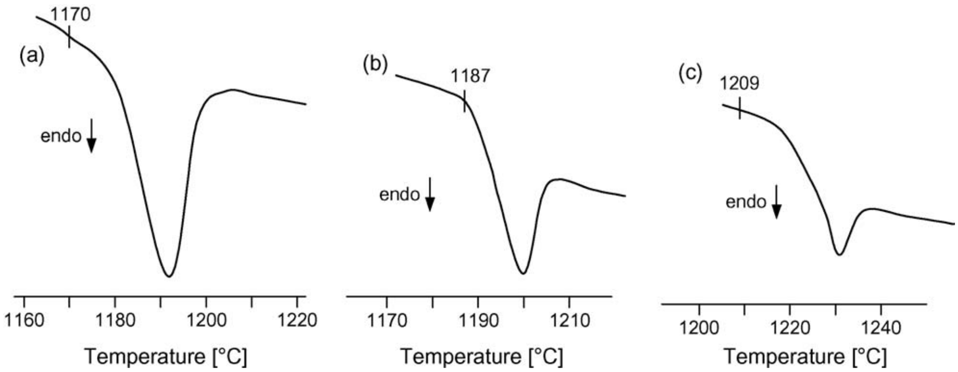

Fig. 3. DTA curves of: (a) $Co_2Sm_2W_3O_{14}$, (b) $Co_2Eu_2W_3O_{14}$ and (c) $Co_2Gd_2W_3O_{14}$ (an inert atmosphere; heating rate, $10\,K\,min^{-1}$).

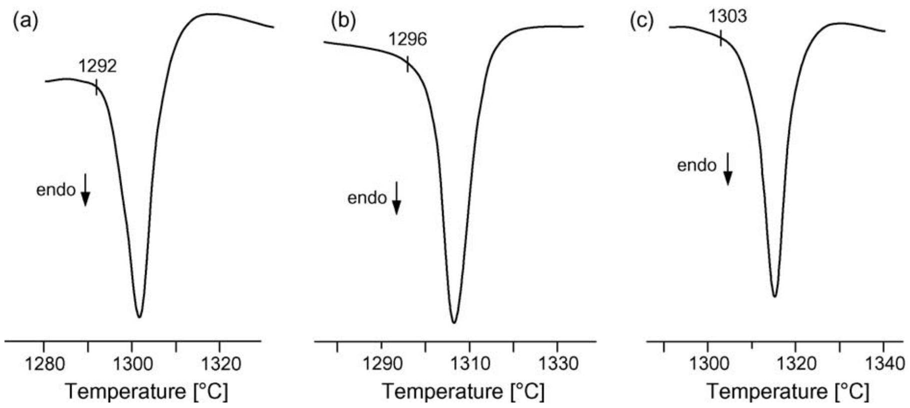

Fig. 4. DTA curves of: (a) $CoSm_4W_3O_{16}$, (b) $CoEu_4W_3O_{16}$ and (c) $CoGd_4W_3O_{16}$ (an inert atmosphere; heating rate, $10\,K\,min^{-1}$).

and XRD examinations. On the base of the XRD analysis it was found that $CoRE_4W_3O_{16}$ samples heated at a temperature above their melting points, i.e. at 1300 °C (Sm), 1310 °C (Eu) or 1315 °C (Gd), contained the corresponding RE_2WO_6 compound. The incongruent melting $CoRE_4W_3O_{16}$ can be described by the following equation:

$$CoRE_4W_3O_{16(s)} \rightarrow RE_2WO_{6(s)} + \text{liquid} \qquad (6)$$

3.2.3. IR spectra

Figs. 5 and 6 show IR spectra of the $Co_2RE_2W_3O_{14}$ and $CoRE_4W_3O_{16}$ compounds, respectively. As it is seen from these figures, the spectra of the $Co_2RE_2W_3O_{14}$ compounds as well as the spectra of the $CoRE_4W_3O_{16}$ phases show a big similarity to each other. In the light of literature information concerning binary and ternary lanthanide tungstates [13], the absorption bands with their maxima at ~850 cm^{-1} ($Co_2RE_2W_3O_{16}$, Fig. 4) and at ~870 cm^{-1} ($CoRE_4W_3O_{16}$, Fig. 5) can be assigned to the stretching mode of W–O bonds in joint WO_6 octahedra. This fact can be confirmed by the presence, in the IR spectra of the $Co_2RE_2W_3O_{14}$ phases as well as in the IR spectra of the $CoRE_4W_3O_{16}$ compounds, of some absorption bands in

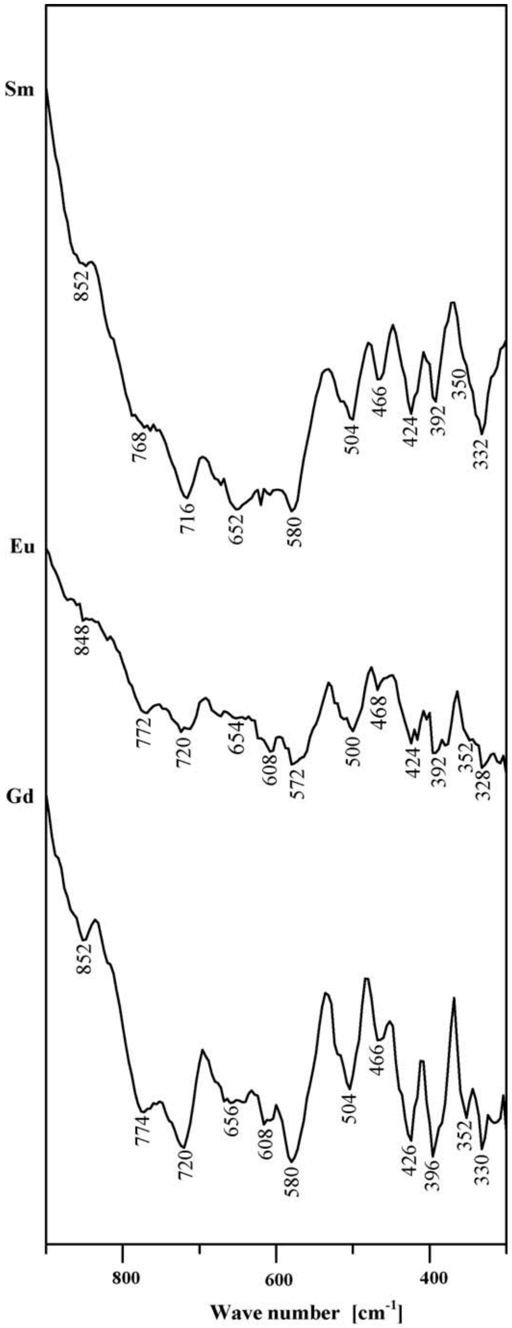

Fig. 5. IR spectra of $Co_2RE_2W_3O_{14}$ compounds.

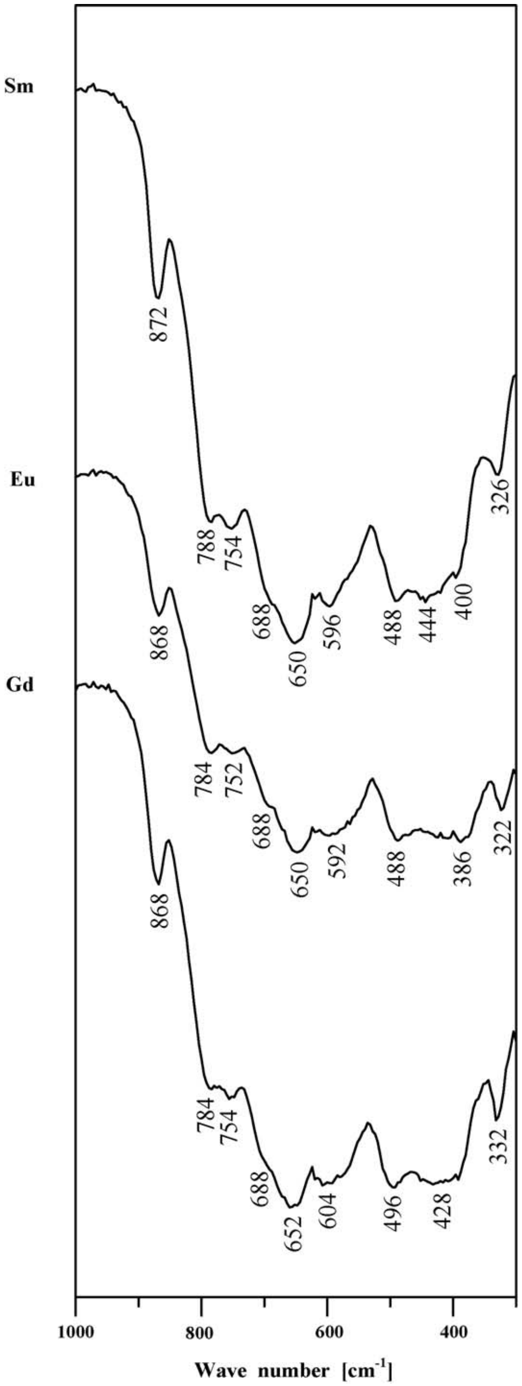

Fig. 6. IR spectra of $CoRE_4W_3O_{16}$ compounds.

the 750–500 cm^{-1} region. Other authors [14–17] suggest that the appearance of absorption bands in this region is caused by the oxygen bridge bond vibrations present in the anion lattice of tungstates, whereas, the absorption bands occurring in the IR spectra of the $Co_2RE_2W_3O_{14}$ and the $CoRE_4W_3O_{16}$ compounds below 500 cm^{-1} can be due to the deformation modes of W–O bonds in WO_6 octahedra or to the deformation modes of W–O–W bridges [14–17].

4. Conclusions

The experimental results obtained have led to the following conclusions:

- $CoWO_4$ and RE_2WO_6 (RE = Sm–Gd) react mutually by heating to give two series of new compounds: $Co_2RE_2W_3O_{14}$ and $CoRE_4W_3O_{16}$,
- the $Co_2RE_2W_3O_{14}$ phases, formed by heating in air $CoWO_4$ and RE_2WO_6 mixed at the molar ratio 2:1, are isostructural,
- the $CoRE_4W_3O_{16}$ compounds, synthesized by heating in air $CoWO_4$ and RE_2WO_6 mixed at the molar ratio 1:2, are isostructural,
- the $CoRE_4W_3O_{16}$ phases are isostructural with $ZnRE_4W_3O_{16}$, published elsewhere [7],
- $Co_2RE_2W_3O_{14}$ and $CoRE_4W_3O_{16}$ crystallize in the orthorhombic system,
- the anion lattice of new cobalt and rare-earth metal tungstates is built by joint WO_6 octahedra,
- the $Co_2RE_2W_3O_{14}$ compounds melt congruently at ~1200 °C,
- the $CoRE_4W_3O_{16}$ phases melt incongruently at ~1300 °C,
- in an inert atmosphere $CoWO_4$ decomposes at ~900 °C, this process is connected with an oxygen evolution and a formation of hitherto unknown $CoWO_{4-x}$.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2006.05.002.

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