

REACTIVITY IN SOLID STATE BETWEEN CdWO_4 AND RE_2WO_6 ($\text{RE}=\text{Y, Nd, Sm, Eu, Gd, Dy, Ho, Er, AND Lu}$)

E.Tomaszewicz¹ and S.M.Kaczmarek²

¹Department of Inorganic and Analytical Chemistry, West Pomeranian University of Technology Al.Piastow 42, 71-065 Szczecin, Poland

²Institute of Physics, West Pomeranian University of Technology, Al.Piastow 17, 70-310 Szczecin, Poland

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Abstract. The reactivity in the solid-state between CdWO_4 and some RE_2WO_6 ($\text{RE}=\text{Y, Nd, Sm, Eu, Gd, Dy, Ho, Er}$) was investigated by the XRD and DTA-TG methods. Eight new cadmium and rare-earths tungstates with the formula $\text{CdRE}_2\text{W}_2\text{O}_{10}$ were synthesized. The obtained compounds were studied using the DTA-TG, IR, and EPR methods.

1. INTRODUCTION

The luminescence of tungstates and molybdates has been studied for a long time [1-18]. Several of these phases, particularly rare-earth compounds, show interesting fluorescence properties and are applied as luminescent materials in several devices. These compounds, used as luminescent films, have played an important role in high-resolution devices such as cathode-ray tubes, electroluminescent devices, plasma display panels and field emission displays [5, 11, 19-23]. Nowadays, the solid-state reaction, the Czochralski and Pechini methods are often used to prepare phosphors in form of powders and single crystals [1, 4, 7, 10, 14-16, 18].

Fedorov and Tunik [24,25] published the results of their investigations concerning the mutual reactivity of CdWO_4 with $\text{RE}_2(\text{WO}_4)_3$ (RE – rare-earth metal). In the CdWO_4 - $\text{La}_2(\text{WO}_4)_3$ system, the authors obtained the compounds: $\text{CdLa}_2(\text{WO}_4)_4$ (the molar ratio of reactants - 1:1) and $\text{CdLa}_4(\text{WO}_4)_7$ (the molar ratio of reactants - 1:2) [26]. The compound with the molar ratio of reactants 1:1 melts congru-

ently as well as the latter phase melts incongruently [26]. Both compounds do not show any homogeneity region [26]. For the lanthanides $\text{RE}=\text{Pr-Ho}$, the authors [24,24] evidenced the existence of families of double tungstates with the following formulas: $\text{Cd}_2\text{RE}_2(\text{WO}_4)_5$ (the molar ratio $\text{CdWO}_4/\text{RE}_2(\text{WO}_4)_3 - 2:1$) and $\text{CdRE}_2(\text{WO}_4)_4$ ($\text{CdWO}_4/\text{RE}_2(\text{WO}_4)_3 - 1:1$). The $\text{Cd}_2\text{RE}_2(\text{WO}_4)_5$ phases crystallize in the scheelite type structure and melt congruently for $\text{RE}=\text{Pr-Eu}$ or incongruently when $\text{RE}=\text{Gd-Ho}$. The $\text{CdRE}_2(\text{WO}_4)_4$ compounds crystallize in a monoclinic system, in a structure very similar to the scheelite type structure [24,25]. When $\text{RE}=\text{Pr-Dy}$, they can form solid state solutions with the $\text{CdRE}_2(\text{WO}_4)_4$ structure [24-26]. The homogeneity region of the $\text{CdRE}_2(\text{WO}_4)_4$ phases is located in the range of about 40-60 mol.% of $\text{RE}_2(\text{WO}_4)_3$ (e.g. 40-60 mol.% for $\text{RE}=\text{Nd}$ or 45-55 mol.% for $\text{RE}=\text{Gd}$) [24,25]. It was also found that the homogeneity region and the thermal stability of $\text{CdRE}_2(\text{WO}_4)_4$ decreased with the decreasing radius of the rare-earth ion [24-26]. The authors [24,25] also ascertained

Corresponding author: E.Tomaszewicz, e-mail: tomela@zut.edu.pl

that solid solutions with the $\text{RE}_2(\text{WO}_4)_3$ type structure were formed at the concentration range up to 20 mol.% of CdWO_4 in initial $\text{CdWO}_4/\text{RE}_2(\text{WO}_4)_3$ mixtures ($\text{RE}=\text{La-Ho}$).

Our earlier studies on the reactivity in the solid state between Pr_2WO_6 and some d-electron metal tungstates with the wolframite structure MWO_4 ($\text{M}=\text{Mn, Co, Cd}$) have shown that these reactants enter into a reaction to give a family of isostructural compounds which has been unknown before: $\text{MPr}_2\text{W}_2\text{O}_{10}$ [27]. These phases crystallize in an orthorhombic system (the unit cell parameters and the values of experimental and calculated density for $\text{CdPr}_2\text{W}_2\text{O}_{10}$ are: $a=0.68567(2)$ nm; $b=1.4586(7)$ nm; $c=0.84102(4)$ nm; $Z=4$; $d_{\text{cal.}}=7.28$ g/cm³; $d_{\text{exp.}}=7.19$ g/cm³) [27]. For $\text{M}=\text{Mn}$ and Co , the $\text{MPr}_2\text{W}_2\text{O}_{10}$ compounds melt incongruently [27]. The cadmium and praseodymium tungstate decomposes in the solid state to $\text{Pr}_2\text{W}_2\text{O}_9$ and gaseous CdO [27].

In this work we carried out investigations concerning a mutual reactivity cadmium tungstate with rare-earth metal tungstates RE_2WO_6 ($\text{RE}=\text{Y, Nd, Sm, Eu, Gd, Dy, Ho, Er, and Lu}$). Particular emphasis was placed on determining the basic properties of the newly obtained $\text{CdRE}_2\text{W}_2\text{O}_{10}$ compounds.

2. EXPERIMENTAL SECTION

2.1. Sample preparation

RE_2WO_6 ($\text{RE}=\text{Y, Nd, Sm, Eu, Gd, Dy, Ho, Er, and Lu}$) were prepared by the conventional solid-state reaction using high purity RE_2O_3 (99.9%, Aldrich) and WO_3 (99.9%, Fluka) as the starting materials. The experimental procedure for a preparation of RE_2WO_6 has been described in our previous papers [27-31]. For the synthesis of CdWO_4 , a stoichiometric mixture of $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ (99%, Aldrich) with WO_3 was homogenized and heated in the following cycles: 1073K (12 h), 1173K (12 h), 1273K (12 h), 1373K (2×12 h). The $\text{CdWO}_4/\text{RE}_2\text{WO}_6$ mixtures were prepared with the range of cadmium tungstate from 10.00 to 90.00 mol.%. The mixtures of CdWO_4 with RE_2WO_6 were heated in air in the following cycles: 1173K (12 hrs), 1223K (12 hrs) 1273K (12 hrs) and 1298K (2×12 hrs). Additionally, the $\text{CdWO}_4/\text{RE}_2\text{WO}_6$ mixtures ($\text{RE}=\text{Y, Dy, Ho, Er}$) were heated in the following temperatures: 1348K (12 hrs) and 1373K (2×12 hrs). Apart from the above mentioned heating stages, the mixtures of CdWO_4 and Lu_2WO_6 were additionally heated for 12 hrs at 1473K and 1523K. After each heating cycle all samples were cooled slowly to the room temperature, weighted, ground and examined for their contents by the XRD method.

2.2. Experimental setup

The powder X-ray diffraction patterns were recorded on a DRON diffractometer using CuK_α radiation ($\lambda=0.15418$ nm). The XRD data were collected by a step-scanning method in the 2θ range from 10° to 45° with a step width of 0.02° and a scan time of 1 s or 10 s.

The DTA-TG measurements were carried out with the Mettler Toledo TGA/SDTA 851 apparatus in the temperature range of 298-1823K, using corundum crucibles, under a continuous nitrogen flow (15 mL min^{-1}) and at the heating rate of 10K min^{-1} .

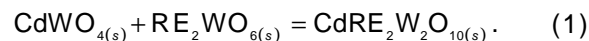
Infrared spectra were recorded on a Specord M-80 spectrometer with a resolution of 4 cm^{-1} . Samples were mixed with KBr and pressed into pellets. The measurements were made at room temperature in the $1500\text{-}300$ cm^{-1} range.

The EPR measurements were performed with a conventional X-band Brücker ELEXSYS E500 CW spectrometer operating at 9.5 GHz with the 100 kHz magnetic field modulation. All the observations were performed with an approximately 0.63 mW microwave power incident upon the sample cavity. Samples of all compounds (~ 30 mg) were placed into 4 mm diameter quartz tubes. The first derivative of the power absorption spectra was recorded as a function of the applied magnetic field. The temperature dependence of the EPR spectra was registered using an Oxford Instruments ESP helium-flow cryostat in the 8-295K temperature range.

3. RESULTS AND DISCUSSION

3.1. Reactivity in the solid state between CdWO_4 and RE_2WO_6

The contents of the $\text{CdWO}_4/\text{RE}_2\text{WO}_6$ initial mixtures and the results of the XRD analysis for all the samples obtained after the last heating period have been collected in Table 1. The experimental results suggest that both reactants enter a reaction to give a series of new cadmium and rare-earth metal tungstates $\text{CdRE}_2\text{W}_2\text{O}_{10}$ ($\text{RE}=\text{Y, Nd, Sm, Eu, Gd, Dy, Ho, and Er}$) according to the following equation:



It was also found that Lu_2WO_6 was inert towards CdWO_4 up to 1523K. On the basis of the XRD analysis of the $\text{CdRE}_2\text{W}_2\text{O}_{10}/\text{RE}_2\text{WO}_6$ mixtures comprising: 2.50; 5.00; 7.50; 10.00; 15.00 and 17.50 mol.% of $\text{CdRE}_2\text{W}_2\text{O}_{10}$ it was ascertained that the detectable amount of $\text{CdRE}_2\text{W}_2\text{O}_{10}$ in the above mixtures with adequate RE_2WO_6 by this method equaled more than 7.50 mol.%. The detection limit of CdWO_4 to

Table 1. Contents of $\text{CdWO}_4/\text{RE}_2\text{WO}_6$ mixtures and results of the XRD analysis of the samples obtained after the final heating stage.

No.	RE_2WO_6 content in $\text{CdWO}_4/\text{RE}_2\text{WO}_6$ mixture [mol %]	Identified phases $\text{RE} = \text{Y, Nd, Sm, Eu, Gd, Dy, Ho, Er}$	Identified phases $\text{RE}=\text{Lu}$
1	10.00	$\text{CdRE}_2\text{W}_2\text{O}_{10}$, CdWO_4	Lu_2WO_6 , CdWO_4
2	20.00		
3	25.00		
4	30.00		
5	33.33		
6	40.00		
7	42.50		
8	45.00		
9	47.50		
10	50.00	$\text{CdRE}_2\text{W}_2\text{O}_{10}$	
11	52.50	$\text{CdRE}_2\text{W}_2\text{O}_{10}$, RE_2WO_6	
12	55.00		
13	57.50		
14	60.00		
15	66.67		
16	70.00		
17	75.00		
18	80.00		
19	82.50		
20	85.00		
21	90.00		
22	92.50	RE_2WO_6 ¹⁾	Lu_2WO_6 ²⁾
23	95.00		
24	97.50		

¹⁾ $\text{CdRE}_2\text{W}_2\text{O}_{10}$ not identified by XRD method

²⁾ CdWO_4 not identified by XRD method

wards Lu_2WO_6 by the XRD method, in the $\text{CdWO}_4/\text{Lu}_2\text{WO}_6$ mixtures, equaled more than 7.50 mol.%, too. No formation of solid solutions with the RE_2WO_6 type structure and the homogeneity region of $\text{CdRE}_2\text{W}_2\text{O}_{10}$ was observed.

3.2. Characteristic of $\text{CdRE}_2\text{W}_2\text{O}_{10}$

3.2.1. Crystallography (from XRD data)

Powder diffraction patterns of $\text{CdRE}_2\text{W}_2\text{O}_{10}$ were subjected to indexing by the POWDER program [32,33]. Table 2 shows the results of the indexing of those compounds. The parameters of $\text{CdRE}_2\text{W}_2\text{O}_{10}$ unit cells and the values of the experimental (obtained by degassing of the samples and hydrostatic weighting in a pycnometric liquid – CCl_4) and theoretical density are tabulated in Table 3.

3.2.2. Thermal properties

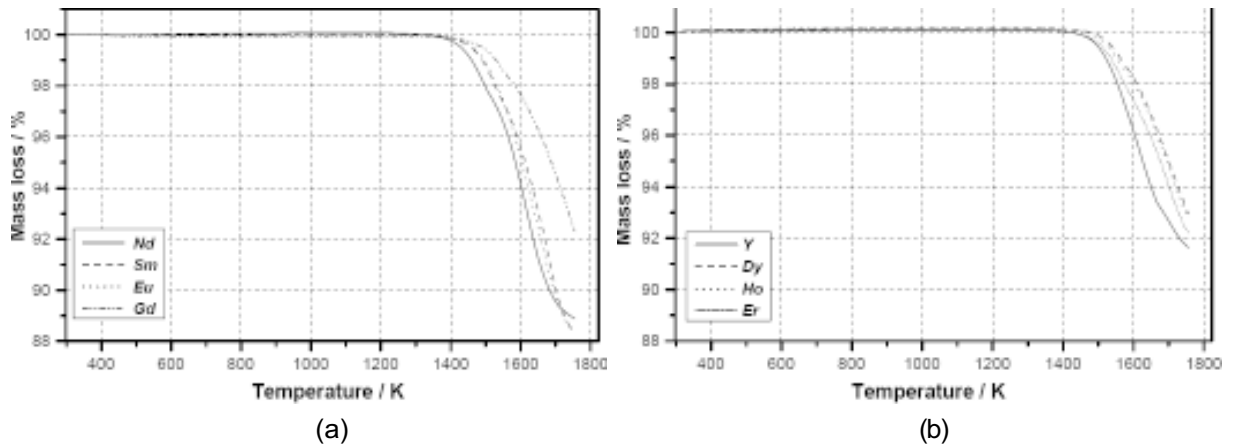
Fig. 1 shows the TG curves of the $\text{CdRE}_2\text{W}_2\text{O}_{10}$ compounds recorded within the temperature range of 298-1823K. The mass loss was recorded on each TG curve of $\text{CdRE}_2\text{W}_2\text{O}_{10}$ starting at 1373K ($\text{RE}=\text{Nd, Sm, Eu, Gd}$) or 1423 K ($\text{RE}=\text{Y, Dy, Ho, Er}$). The mass losses observed at 177K are: 8.365% (Y); 11.117% (Nd); 11.638% (Sm); 11.659%(Eu); 7.706% (Gd); 7.058% (Dy); 7.265% (Ho); 7.805% (Er). On the basis of the TG studies and the observation of the residue arising in the crucibles after these experiments it was found that the $\text{CdRE}_2\text{W}_2\text{O}_{10}$ compounds were not melted. Samples of these phases were heated in a furnace at 1573K for 4 h. After heating the samples were quickly removed from the furnace and quenched to 263K. The results of an XRD analysis conducted for these samples showed that they contained $\text{RE}_2\text{W}_2\text{O}_9$ ($\text{RE}=\text{Nd, Sm, Eu, Gd}$)

Table 2. Results of indexing CdRE₂W₂O₁₀ (RE=Y, Nd, Sm, Eu, Gd, Dy, Ho, Er) powder diffraction patterns.

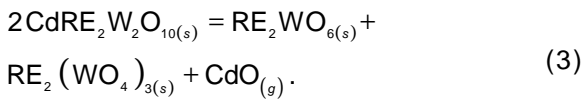
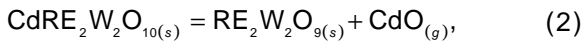
No.	Y		Nd		Sm		Eu		Gd		Dy		Ho		Er		h	k	l
	<i>d</i> _{obs} [nm]	// <i>l</i> ₀	<i>d</i> _{obs} [nm]	// <i>l</i> ₀	<i>d</i> _{obs} [nm]	// <i>l</i> ₀	<i>d</i> _{obs} [nm]	// <i>l</i> ₀	<i>d</i> _{obs} [nm]	// <i>l</i> ₀	<i>d</i> _{obs} [nm]	// <i>l</i> ₀	<i>d</i> _{obs} [nm]	// <i>l</i> ₀	<i>d</i> _{obs} [nm]	// <i>l</i> ₀			
1	0.47501	5	0.48452	4	0.48113	4	0.47959	5	0.47754	5	0.47652	5	0.47526	6	0.47450	5	0	1	0
2	0.46490	4	0.47805	3	0.47627	3	0.47400	3	0.47150	4	0.46757	5	0.46562	5	0.46417	4	0	0	2
3	0.44996	2	0.46083	2	0.45777	2	0.45660	2	0.45568	2	0.45223	2	0.45064	2	0.44906	2	1	0	2
4	0.37185	2	0.38063	2	0.37840	2	0.37666	2	0.37494	2	0.37370	2	0.37231	2	0.37094	2	1	1	1
5	0.36187	5	0.36912	3	0.36612	4	0.36553	4	0.36494	4	0.36333	3	0.36216	4	0.36144	4	2	0	2
6	0.30727	100	0.31296	100	0.31062	100	0.31030	100	0.30977	100	0.30883	100	0.30800	100	0.30686	100	3	0	1
7	0.30460	92	0.31104	75	0.30914	90	0.30800	92	0.30748	87	0.30655	86	0.30542	90	0.30400	96	3	0	0
8	0.29941	3	0.30748	2	0.30573	3	0.30420	3	0.30299	4	0.30119	7	0.30000	10	0.29902	6	1	1	2
9	0.29785	6	0.30491	3	0.30319	5	0.30169	6	0.30060	5	0.29961	4	0.29814	5	0.29718	4	2	1	1
10	0.28036	2	0.28640	22	0.28586	3	0.28330	3	0.28269	3	0.28139	7	0.28070	7	0.27994	6	3	0	2
11	0.27765	21	0.28524	10	0.28295	22	0.28217	26	0.28157	24	0.27968	23	0.27816	28	0.27682	28	1	0	3
12	0.26084	20	0.26641	16	0.26564	14	0.26481	15	0.26345	14	0.26195	18	0.26143	20	0.26062	23	1	1	3
13	0.25801	3	0.26285	20							0.25916	4	0.25851	4	0.25779	4	3	1	1
14	0.25651	2	0.26180	15	0.26018	20	0.25909	22	0.25895	21	0.25786	21	0.25700	22	0.25608	20	3	1	0
15			0.25967	13													2	1	2
16	0.24283	2	0.24800	2	0.24623	2	0.24552	2	0.24493	2	0.24359	2	0.24257	2	0.24245	2	2	1	3
17	0.22502	2					0.22824	2	0.22731	2	0.22610	2	0.22545	2	0.22464	2	2	0	4
18	0.22075	1			0.22389	2	0.22283	2	0.22226	2	0.22163	2	0.22095	2	0.22049	2	1	2	1
19	0.21147	3			0.21472	2	0.21404	3	0.21308	2	0.21232	2	0.21170	2	0.21123	3	0	2	2

Table 3. The parameters of CdRE₂W₂O₁₀ unit cells and the values of experimental and calculated density.

	<i>a</i> /nm	<i>b</i> /nm	<i>c</i> /nm	β /°	<i>Z</i>	<i>V</i> /nm ³	<i>a</i> / <i>b</i>	<i>c</i> / <i>b</i>	<i>d</i> _{exp} /g/cm ³	<i>d</i> _{rig} / g/cm ³
CdY ₂ W ₂ O ₁₀	0.93082(9)	0.47518(1)	0.94639(4)	100.95(3)	2	0.41097(7)	1.9589	1.9916	6.61	6.62
CdNd ₂ W ₂ O ₁₀	0.94879(4)	0.48462(2)	0.97275(8)	100.38(8)	2	0.43994(8)	1.9578	2.0073	7.10	7.01
CdSm ₂ W ₂ O ₁₀	0.94219(2)	0.48099(9)	0.96853(2)	100.13(5)	2	0.43208(3)	1.9588	2.0136	7.32	7.23
CdEu ₂ W ₂ O ₁₀	0.93849(3)	0.47952(1)	0.96370(9)	100.48(6)	2	0.42645(2)	1.9571	2.0097	7.39	7.35
CdGd ₂ W ₂ O ₁₀	0.93927(2)	0.47788(6)	0.95830(5)	100.66(3)	2	0.42272(2)	1.9655	2.0053	7.54	7.50
CdDy ₂ W ₂ O ₁₀	0.93597(9)	0.47664(2)	0.95169(8)	100.71(1)	2	0.41718(3)	1.9637	1.9967	7.72	7.68
CdHo ₂ W ₂ O ₁₀	0.93284(7)	0.47538(1)	0.94779(4)	100.86(6)	2	0.41277(1)	1.9623	1.9938	7.83	7.78
CdEr ₂ W ₂ O ₁₀	0.92931(2)	0.47471(6)	0.94440(1)	101.03(8)	2	0.40892(4)	1.9576	1.9894	7.90	7.91


Fig. 1. TG curves of $CdRE_2W_2O_{10}$.

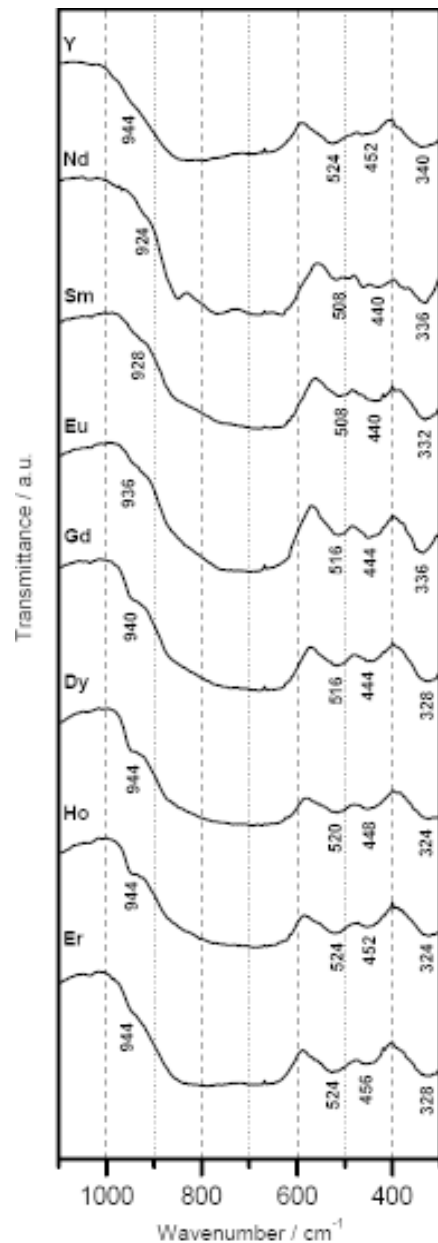
or $RE_2(WO_4)_3$ and RE_2WO_6 ($RE=Y, Dy, Ho, Er$). Therefore, the decomposition of $CdRE_2W_2O_{10}$ in the solid-state can be described as the following processes:



The calculated values of mass losses in case of Eqs. (2) and (3) are: 15.661% (Y); 13.829% (Nd); 13.649% (Sm); 13.602% (Eu); 13.452% (Gd); 13.305% (Dy); 13.280% (Ho); 13.175% (Er). The experimental values are lower than the calculated ones. It means that the decomposition process of $CdRE_2W_2O_{10}$ was not finished under the DTA-TG studies. Endothermic effects connected with melting of $RE_2W_2O_9$ (the temperature range of 1475(Gd)-1611(Nd) K [34]) or $RE_2(WO_4)_3$ (the temperature range of c.a. 1598(Dy)-1773(Er) K [26]) were not observed on the DTA curves (not presented) of the obtained compounds. The RE_2WO_6 compounds melt above 1773K [26].

3.2.3. IR spectra

Fig. 2 shows the IR spectra of $CdRE_2W_2O_{10}$. As is seen from Fig. 2, the spectra of the obtained compounds show a high similarity to each other. In the light of the literature information concerning primary, binary and ternary rare-earths tungstates with different coordination of W^{6+} by oxygen ions, the absorption bands with their maxima located at 944-924 cm^{-1} range could be related to the symmetric stretching modes of WO_4 [35-39].


Fig. 2. IR spectra of $CdRE_2W_2O_{10}$.

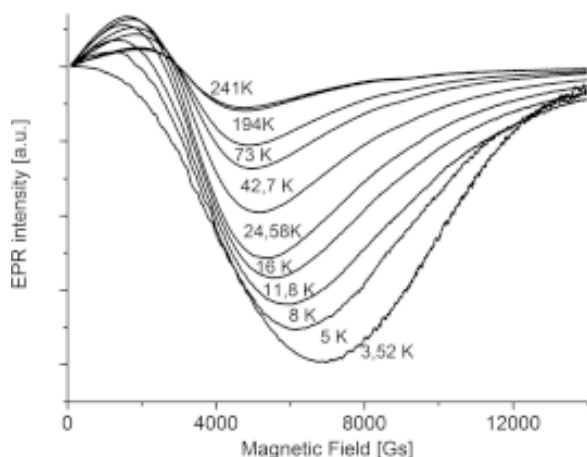


Fig. 3. EPR resonance lines of an initial, equimolar $\text{CdWO}_4/\text{Gd}_2\text{WO}_6$ mixture for several selected temperatures.

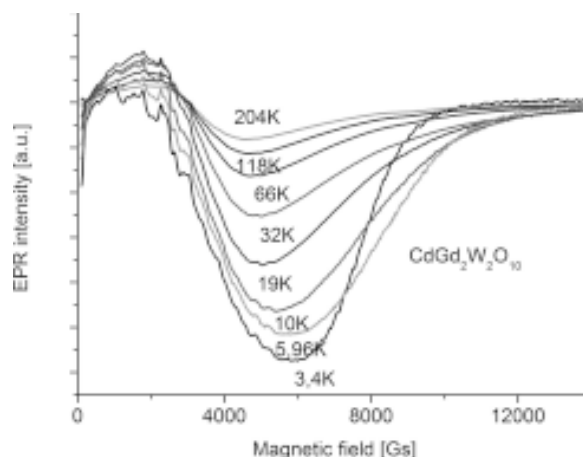


Fig. 4. EPR resonance lines of a $\text{CdGd}_2\text{W}_2\text{O}_{10}$ compound for several selected temperatures.

On the other hand, the very broad absorption bands centered on 750 cm^{-1} are due to the asymmetric stretching vibrations of W-O in WO_4 tetrahedra [36-39]. Then again, the absorption bands with their maxima located below 600 cm^{-1} can be assigned to the symmetric or asymmetric modes of W-O in WO_4 [36-39]. A small shift of the maxima of the absorption bands observed while the rare-earth ion radius decreases is associated with the decreasing interatomic W-O distances.

3.2.4. EPR spectra

Two samples, powders of a $\text{CdWO}_4/\text{Gd}_2\text{WO}_6$ mixture and a $\text{CdGd}_2\text{W}_2\text{O}_{10}$ compound were investigated using the X-band EPR spectroscopy in a wide temperature range.

In Fig. 3 the EPR spectra of an initial, equimolar $\text{CdWO}_4/\text{Gd}_2\text{WO}_6$ mixture are presented. As can be seen, in temperature range of 3.5-240K, the spectra consist of a wide and intense signal.

Fig. 4 presents the EPR results for the second $\text{CdGd}_2\text{W}_2\text{O}_{10}$ compound. The resonance spectrum of this sample consists of a wide line and an additional, slight but clear fine structure observed in a temperature range below 30K.

The observed spectrum seems to be determined by the fine structure, being really an envelope of an unresolved anisotropic fine structure in powder. Taking into account both figures we found that there also existed some exchange interactions between Gd^{3+} ions leading to the formation of complex Gd^{3+} magnetic centers. Hence, we are dealing here with

the influence of the exchange interactions on the fine structure. The very wide and intense resonance line observed for both samples could be ascribed to clusters or low dimensional chains with antiferromagnetic type of interactions [40]; whereas the origin of the fine structure, observed for the $\text{CdGd}_2\text{W}_2\text{O}_{10}$ compound, may be isolated paramagnetic Gd^{3+} ions. This conclusion seems to be consistent with other reports concerning trivalent gadolinium sites. For example Kliava et al. [41] found that well resolved features of the EPR spectrum excluded clustering for Gd^{3+} ions in oxide glasses. When the amount of gadolinium ions increased, in addition to a slightly resolved signal due to isolated Gd^{3+} ions, a broad resonance line with $g_{\text{eff}}=2.25$ was observed. This latter signal was ascribed to clusters of Gd^{3+} ions, linked with each other through the oxygen bridges. Hence, the slightly resolved shape of the EPR spectrum observed for the $\text{CdGd}_2\text{W}_2\text{O}_{10}$ compound may be due to a lower content of gadolinium ions in the $\text{CdGd}_2\text{W}_2\text{O}_{10}$ compound with respect to the $\text{CdWO}_4/\text{Gd}_2\text{WO}_6$ mixture, while the broad EPR line observed for both compounds may be due to the presence of gadolinium clusters or to magnetic species of higher complexity.

Cd^{2+} is a diamagnetic ion which can nevertheless change the magnetic properties of some compounds increasing, e.g., the concentration of free radicals and fasten spin relaxation processes. It was also found that dipolar interactions between paramagnetic centres existing in complexes with Cd^{2+} were stronger than in crude ones [42].

4. CONCLUSIONS

Eight new compounds with the formula: $CdRE_2W_2O_{10}$ ($RE = Y, Nd, Sm, Eu, Gd, Dy, Ho, \text{ and } Er$) were prepared by the conventional solid-state technique. The full structure of these materials is still unknown, but the XRD measurements suggest its low symmetry. The obtained phases are isostructural and crystallize probably in a monoclinic system. The cell volume of the analyzed phases decreases when the rare-earth ion radius decreases (Table 3).

The $CdRE_2W_2O_{10}$ compounds undergo decomposition in the solid state, where the final solid products are: $RE_2W_2O_9$ or $RE_2(WO_4)_3$ and RE_2WO_6 . We suggest that the anion lattice of $CdRE_2W_2O_{10}$ compounds is built by WO_4 tetrahedra.

The EPR results for the $CdWO_4/Gd_2WO_6$ mixture and the $CdGd_2W_2O_{10}$ compound show that Gd^{3+} ions create extended magnetic systems i.e. clusters or low dimensional chains. For the new materials analyzed in the paper, it seems necessary to do detailed resolving of the crystal structure. Detailed information about the structure could be useful in the description of Gd^{3+} magnetic species and the type of their magnetic interactions.

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