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REACTIVITY IN THE SOLID-STATE BETWEEN $ZnWO_4$ AND SOME RARE-EARTH METAL MOLYBDATES RE_2MoO_6 (*RE*=Y, Sm, Eu, Gd, Dy, Ho, Er and Lu)

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Reactivity in the solid-state between $ZnWO_4$ and some RE_2MoO_6 (*RE*=Y, Sm, Eu, Gd, Dy, Ho, Er and Lu) was investigated by XRD and DTA-TG methods. Four new compounds with the formula $ZnRE_2MoWO_{10}$ (*RE*=Sm, Eu, Gd, Dy) were synthesized. The obtained compounds are isostructural and crystallize in the monoclinic system. They melt incongruently within the temperature range of 1016–1033°C. The solid product of melting is an adequate of rare-earths molybdate.

Keywords: *DTA-TG, rare-earth metal molybdates, reactivity in the solid-state, zinc tungstate*

Introduction

Nowadays, the solid-state chemistry of mixed-metal oxides containing both rare-earths and *d*-electron metals (4*d*, 5*d* or/and 6*d*) has attracted a great deal of interest. These inorganic materials adopt a diverse range of structures and show a wide range of electronic properties. Rare-earth compounds have been widely used in high-performance luminescent devices, magnets, photocatalysts, pigments [1–10] and other functional materials owing to the numerous well-defined transitions modes concerning the 4*f* shell of their ions. Thus, in recent years, more and more interest has been put in a synthesis and a photoluminescence of new rare-earths compounds.

It was reported that zinc tungstate ($ZnWO_4$) reacted with some rare-earth metal tungstates (RE_2WO_6) to give the family of isostructural compounds with the general formula $ZnRE_4W_3O_{16}$ (*RE*=Y, Nd, Sm, Eu, Gd, Dy and Ho) [11]. These compounds were synthesized in air, by the solid-state reaction technique at high temperatures from appropriate $ZnWO_4/RE_2WO_6$ mixtures according to the following reaction [11]:

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

$ZnRE_4W_3O_{16}$ crystallize in the orthorhombic system. These compounds melt incongruently or decompose in the solid-state above 1250°C [11]. The excitation and emission spectra under 613 nm excitation for $ZnEu_4W_3O_{16}$ showed that this compound could be potentially attractive as phosphor [11]. Therefore we have focused our attention on obtaining other rare-earth compounds with interesting photoluminescent properties.

In the present work, the reactivity in the solid-state of $ZnWO_4$ towards some RE_2MoO_6 (*RE*=Y, Sm, Eu, Gd, Dy, Ho, Er and Lu) has been studied. The new compounds $ZnRE_2MoWO_{10}$ (*RE*=Sm, Eu, Gd and Dy) have been examined by powder X-ray diffraction (XRD), thermal analysis (DTA-TG) and infrared spectroscopy (IR).

Experimental

Sample preparation

The starting materials were $ZnWO_4$ and RE_2MoO_6. Both compounds were synthesized by conventional ceramic method used by us in our earlier studies [12, 13]. An equimolar mixture of $ZnSO_4{\cdot}7H_2O$ (99.99%, POCh-Poland) with WO_3 (99.99%, Aldrich) was heated in air at the following cycles: 600°C (12 h); 800°C (12 h); 900°C (12 h); 1000°C (12 h) and 1100°C (12 h). RE_2MoO_6 were prepared by heating RE_2O_3 (all oxides with a purity 99.9%, Aldrich) and MoO_3 (99.9%, POCh-Poland) mixed at the molar ratio 1:1. The RE_2O_3/MoO_3 mixtures were heated in the following heating cycles: 650°C (12 h); 700°C (12 h); 750°C (12 h); 800°C (12 h); 900°C (12 h) and 1000°C (2·12 h).

The mixtures of $ZnWO_4$ with RE_2MoO_6 were prepared with the range of rare-earths molybdate from 20.00 to 80.00 mol%. These mixtures were heated in air, in the following periods: 900°C (12 h); 925°C (12 h); 950°C (12 h); 970°C (12 h) and 980°C (12 h). Additionally, the $ZnWO_4/RE_2MoO_6$ mixtures (*RE*=Y, Ho, Er, Lu) were heated at 1000°C (12 h) and 1025°C (12 h). After each heating cycle, the samples were

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cooled gradually to ambient temperature, ground and analyzed by XRD. After the final heating period the samples were examined by DTA-TG and IR methods.

Characterization experimental methods

Routine phase analysis was conducted with a DRON-3 diffractometer using the $CuK_{\alpha_{aver.}}$ radiation (λ=0.15418 nm). Diffraction patterns were collected within the 2Θ range 10–45°, at the stepped scan rate 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. The scans were performed in the same conditions.

DTA-TG examinations were carried out using a Mettler Toledo TGA/SDTA851 apparatus. These measurements were performed within the temperature range of 20–1300°C, in a nitrogen atmosphere (gas flow 15 mL min^{-1}), using corundum crucibles and at the heating rate of 10 K min^{-1}. The mass of each samples was ~100 mg.

Table 1 Contents of $ZnWO_4/RE_2MoO_6$ mixtures and results of XRD analysis of samples obtained after the final heating stage

	RE_2MoO_6 content in $ZnWO_4$/ RE_2MoO_6 mixture/mol %	Identified phases *RE*=Sm, Eu, Gd, Dy	Identified phases *RE*=Y, Ho, Er, Lu
1	20.00	$ZnRE_2MoWO_{10}$, $ZnWO_4$	$ZnWO_4$, RE_2WO_6, $RE_2(MoO_4)_3$[a]
2	25.00		
3	33.33		
4	40.00		
5	42.50		
6	45.00		
7	47.50		
8	50.00	$ZnRE_2MoWO_{10}$,	RE_2WO_6, $RE_2(MoO_4)_3$, $ZnWO_4$, ZnO
9	52.50		
10	55.00		
11	57.50	$ZnRE_2MoWO_{10}$, RE_2MoO_6	RE_2WO_6, $RE_2(MoO_4)_3$, ZnO[b]
12	60.00		RE_2WO_6, $RE_2(MoO_4)_3$, ZnO
13	66.67		RE_2WO_6, $RE_2(MoO_4)_3$, ZnO, RE_2MoO_6
14	75.00		RE_2WO_6, $RE_2(MoO_4)_3$, RE_2MoO_6[a]
15	80.00		

[a] ZnO not identified by XRD method
[b] $ZnWO_4$ not identified by XRD method

The IR spectra were recorded on a Specord M-80 spectrometer (Carl Zeiss Jena). The samples were pressed in pellets with KBr at the mass ratio of 1:300.

The density of obtained compounds was determined by degassing the samples and hydrostatic weighing in an pycnometric liquid (CCl_4).

Results and discussion

Reactivity in the solid-state between RE_2MoO_6 and $ZnWO_4$

Table 1 shows the contents of initial $ZnWO_4$/ RE_2MoO_6 mixtures and the results of XRD analysis for the samples obtained after the last heating these mixtures. The data in Table 1 indicate that initial components of $ZnWO_4/RE_2MoO_6$ mixtures were not mutually inert in air. When *RE*=Sm, Eu, Gd and Dy these compounds react to give series of unknown up to then compounds with the formula $ZnRE_2MoWO_{10}$.

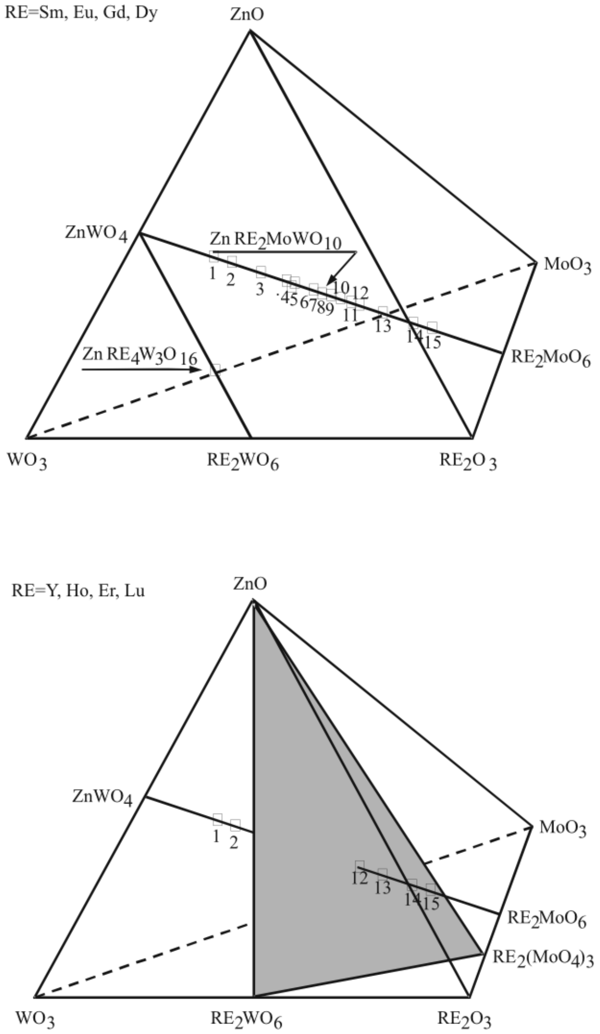

Fig. 1 Concentration tetrahedra of the $ZnO–MoO_3–WO_3–RE_2O_3$ system

The obtained compounds are formed in the following reactions:

$$ZnWO_{4(s)}+RE_2MoO_{6(s)}=ZnRE_2MoWO_{10(s)} \quad (2)$$

For the small rare-earth ions (*RE*=Y, Ho, Er and Lu) the reaction of zinc tungstate with rare-earths molybdates can be described by the Eq. (3):

$$2ZnWO_{4(s)}+3RE_2MoO_{6(s)}= \\ 2RE_2WO_{6(s)}+RE_2(MoO_4)_{3(s)}+2ZnO_{(s)} \quad (3)$$

Concentration tetrahedra of the $ZnO–MoO_3–WO_3–RE_2O_3$ system with the positions of the initial $ZnWO_4/RE_2WO_6$ mixtures, the position of the $ZnRE_4W_3O_{16}$ and $ZnRE_2MoWO_{10}$ phases as well as the triangle $ZnO–RE_2WO_6–RE_2(MoO_4)_3$ are showed in Fig. 1.

Crystallography (from XRD data)

The powder diffraction patterns of the $ZnRE_2MoWO_{10}$ compounds were subjected to indexing procedure. First successive diffraction lines recorded within 2Θ (CuK_α) 10–45° region were selected for indexing performed by means of the POWDER program [14, 15]. Results of indexing the diffraction lines recorded on the diffraction patterns of $ZnRE_2MoWO_{10}$ have been presented in Table 2. The values of parameters of the unit cells as well as the values of experimental and calculated density for the new compounds have been showed in Table 3. The calculated values of the ab^{-1} and cb^{-1} ratios of cell parameters have been presented in Table 3, too. The obtained phases are isostructural and crystallize in the monoclinic system.

Table 2 Results of indexing $ZnRE_2MoWO_{10}$ (*RE*=Sm, Eu, Gd, Dy) powder diffraction patterns

No.	$ZnSm_2MoWO_{10}$			$ZnEu_2MoWO_{10}$			$ZnGd_2MoWO_{10}$			$ZnDy_2MoWO_{10}$			*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	d_{obs}/ nm	d_{cal}/ nm	100 I/I_0			
1	2	3	4	5	6	7	8	9	10	11	12	13		14	
1	0.59743	0.59735	3	0.59504	0.59491	4	0.59345	0.59362	3	0.59022	0.59012	3	0	1	1
2	0.47476	0.47473	3	0.47325	0.47286	3	0.47176	0.47148	3	0.46854	0.46851	3	0	3	1
3	0.45965	0.45969	1	0.45800	0.45803	1	0.45637	0.45624	1	0.45314	0.45312	2	1	3	0
4	0.39202	0.39202	2	0.39066	0.39033	1	0.38948	0.38903	2	0.38667	0.38620	2	1	2	1
5	0.37428	0.37445	2	0.37320	0.37320	2	0.37181	0.37207	2	0.36957	0.36997	2	1	3	$\bar{1}$
6	0.36877	0.36869	2	0.36727	0.36734	2	0.36579	0.36580	2	0.36318	0.36325	2	0	6	0
7				0.36314	0.36291	1							1	3	1
8	0.36039	0.36022	5	0.35996	0.35884	4	0.35810	0.35760	5	0.35617	0.35525	4	0	5	1
9	0.33406	0.33409	1	0.33260	0.33271	1	0.33126	0.33153	1	0.32903	0.32914	1	1	4	1
10	0.31606	0.31602	9	0.31486	0.31487	9	0.31356	0.31354	9	0.3115	0.31136	8	0	7	0
11	0.31025	0.31020	100	0.30898	0.30892	100	0.30825	0.30830	100	0.30634	0.30651	100	0	0	2
12	0.30721	0.30719	2	0.30608	0.30593	3	0.30526	0.30530	2	0.30349	0.30352	2	0	1	2
13	0.30424	0.30431	2	0.30243	0.30308	1	0.30163	0.30197	1	0.29951	0.29980	1	1	5	1
14	0.28589	0.28593	3	0.28483	0.28477	4	0.28403	0.28411	5	0.28208	0.28240	4	0	3	2
15	0.28412	0.28410	15	0.28316	0.28308	17	0.28211	0.28201	15	0.28011	0.28011	14	2	2	0
16	0.28151	0.28159	8	0.28056	0.28054	6	0.27953	0.27949	2				0	7	1
17	0.27298	0.27306	2	0.27201	0.27208	2	0.27089	0.27105	1	0.26921	0.26921	2	2	3	0
18	0.26836	0.26835	1				0.26658	0.26644	1				1	1	2
19	0.26197	0.26179	23	0.26108	0.26094	25	0.26019	0.26010	25	0.25858	0.25859	26	2	2	$\bar{1}$
20	0.25968	0.25957	9										2	4	0
21				0.24761	0.24789	9	0.24722	0.24726	8	0.24617	0.24591	9	1	4	$\bar{2}$
22	0.24689	0.24688	9	0.24591	0.24588	1	0.24500	0.24497	1	0.24327	0.24317	2	2	3	1
23	0.24220	0.24223	1	0.24138	0.24143	2	0.24057	0.24061	1	0.23909	0.23946	2	2	4	1
24	0.22980	0.22984	2	0.22902	0.22902	3	0.22813	0.22812	2	0.22654	0.22656	2	2	6	0
25	0.22544	0.22544	3	0.22463	0.22454	3	0.22378	0.22369	2	0.22210	0.22206	2	2	5	$\bar{1}$
26	0.21803	0.21801	1	0.21723	0.21710	1	0.21648	0.21641	2	0.21497	0.21492	1	1	6	2
27	0.21360	0.21357	1	0.21273	0.21272	1	0.21192	0.21191	1	0.21039	0.21038	1	2	6	1

Table 3 Calculated parameters of the $ZnRE_2MoWO_{10}$ unit cells and the values of experimental and calculated density

Compound (colour)	*a*/nm	*b*/nm	*c*/nm	β/°	ab^{-1}	cb^{-1}	*V*/nm^3	*Z*	$\rho_{exp.}$/ g cm^{-3}	$\rho_{cal.}$/ g cm^{-3}
$ZnSm_2MoWO_{10}$ (yellow)	0.58829 (9)	2.2121 (5)	0.62080(4)	92.074 (8)	0.2659	0.2806	0.80739 (0)	4	6.59	6.63
$ZnEu_2MoWO_{10}$ (bright yellow)	0.58621 (8)	2.2040 (6)	0.61827(5)	92.1407 (7)	0.2660	0.2805	0.79829 (0)	4	6.70	6.73
$ZnGd_2MoWO_{10}$ (bright yellow)	0.58404 (7)	2.1948 (0)	0.61704(5)	92.175 (0)	0.2661	0.2811	0.79040 (1)	4	6.92	6.89
$ZnDy_2MoWO_{10}$ (bright yellow)	0.58015 (5)	2.1795 (0)	0.61350(8)	92.299 (0)	0.2662	0.2815	0.77512 (5)	4	7.05	7.11

Thermal properties

Figure 2 shows DTA curves of $ZnRE_2MoWO_{10}$. On each DTA curve only one endothermic effect was recorded up to 1300°C. No mass losses were recorded on the TG curves (not presented) up the onset of the observed effects on the DTA curves. On the base of the DTA-TG examinations and our observations of residues after these experiments it was found that the $ZnRE_2MoWO_{10}$ compounds melt at: *Sm* – 1021°C, *Eu* – 1028°C, *Gd* – 1033°C and *Dy* – 1016°C. In order to determine melting behavior of these phases additional experiments have made. Samples of $ZnRE_2MoWO_{10}$ were heated in a furnace at the temperatures higher than the onset of the recorded endothermic effects. After heating for 4 h the samples were quickly removed from a furnace and quenched to –10°C. The XRD analysis made for the samples obtained this way showed that they contained an adequate rare-earth metal molybdate. Thus, the incongruent melting the $ZnRE_2MoWO_{10}$ compounds can be described by the following equation:

$$ZnRE_2MoWO_{10(s)} \rightarrow RE_2MoO_{6(s)} + \text{liquid} \qquad (4)$$

Endothermic effects connected with melting RE_2MoO_6 were not observed on the DTA curves of $ZnRE_2MoWO_{10}$ because the RE_2MoO_6 phases melt within the temperature range of 1700–1900°C [16, 17].

IR spectra

Figure 3 shows IR spectra of the $ZnRE_2MoWO_{10}$ phases. As it is seen from this figure, the spectra of obtained compounds show big similarity to each other. Based on the literature information concerning primary, binary and ternary rare-earths or indium molybdates and tungstates with tetrahedral and octahedral coordination of Mo^{6+} and W^{6+} by oxygen ions [18–24], the absorption bands with their maxima at: 940 (*Sm*) and 944 cm^{-1} (*Eu*, *Gd*, *Dy*) as well as at 920 (*Sm*, *Eu*) and 922 cm^{-1} (*Gd*, *Dy*) could be assigned to the symmetric stretching modes of Mo–O bonds in

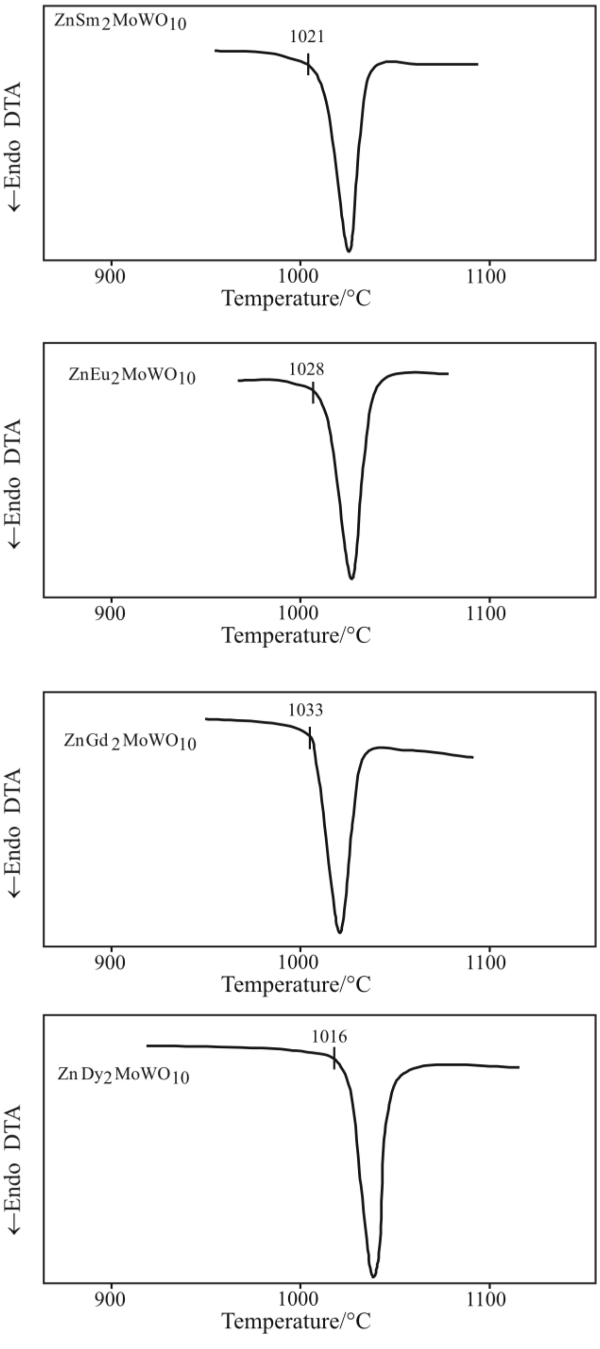

Fig. 2 DTA curves of the $ZnRE_2MoWO_{10}$ compounds

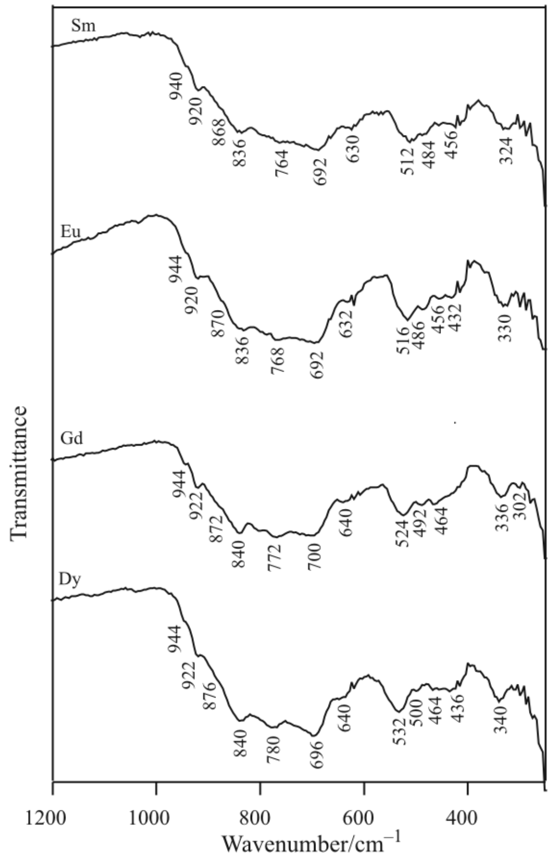

Fig. 3 IR spectra of the $ZnRE_2MoWO_{10}$ compounds

isolated MoO_4 tetrahedra [18, 19, 21]. The stretching vibrations of short therminal Mo–O bonds in MoO_4 tetrahedra were observed in IR spectra of the $BaRE_2(MoO_4)_4$ (*RE*=Ce–Dy), $Tl_5A_{0.5}Hf_{1.5}(MoO_4)_6$ (*A*=Ca, Sr, Ba, Pb) and $KRE(MoO_4)_2$ compounds (the region of vibration frequencies 950–922 cm^{-1}) [18, 19, 21]. On the other hand, the absorption bands with the maxima at: 868 cm^{-1} (*Sm*), 870 cm^{-1} (*Eu*), 872 cm^{-1} (*Gd*) and 876 cm^{-1} (*Dy*) (Fig. 3) could be due to the stretching modes of W–O bonds in joint WO_6 octahedra forming structure elements $[(W_2O_9)^{6-}]\infty$. The stretching vibrations of W–O bonds in structure elements $[(W_2O_9)^{6-}]\infty$ were observed in IR spectra of $RE_2W_2O_9$ (*RE*=Pr–Gd, the region of vibration frequencies 885–867 cm^{-1} [18, 20]). Again, the broad absorption bands with their maxima at: 836, 764, 692, 630 cm^{-1} (*Sm*); 836, 768, 692, 632 cm^{-1} (*Eu*); 840, 772, 700, 640 cm^{-1} (*Gd*); 840, 780, 696, 640 cm^{-1} (*Dy*) could be assigned to the asymmetric stretching vibrations of W–O bonds in joint octahedra WO_6 as well as to the oxygen double bridge bonds WOOW [20, 22]. On the other hand it is known that the region of vibration frequencies below 850 cm^{-1} is characteristic for asymmetric stretching vibrations of Mo–O in MoO_4 [21]. The authors suggest that the weak absorption bands with their maxima at 640, 632 or 630 cm^{-1} (Fig. 3) could be connected with vibrations of Zn–O bonds in unknown ZnO_x polyhedra. The absorption bands found in IR spectra below ~530 cm^{-1} can be assigned to the symmetric and also asymmetric deformation modes of W–O in joint WO_6 octahedra, to the deformation modes of the oxygen bridges WOOW as well as to the symmetric and asymmetric vibrations of Mo–O bonds in MoO_4 tetrahedra [20–24].

Conclusions

Four new compounds with the formula $ZnRE_2MoWO_{10}$ (*RE*=Sm, Eu, Gd and Dy) were prepared by the solid-state reaction technique at high temperatures. The above mentioned compounds are isostructural and crystallize in the monoclinic system. The cell volume of all compounds decreases when rare-earth ion radius decreases (Table 3). The calculated values of the ratios of cell parameters ab^{-1} and cb^{-1} (Table 3) are ~0.2660 and ~0.2810, respectively. These values could suggest that the $ZnRE_2MoWO_{10}$ compounds had probably layered structure. All compounds melt incongruently within the temperature range 1016–1033°C. The solid product of melting is an adequate of rare-earths molybdate. The IR spectra of the $ZnRE_2MoWO_{10}$ compounds are difficult to an interpretation in consideration of absence of information concerning the structure of above mentioned phases. However, the authors suggest the presence of isolated MoO_4 tetrahedra and the structure elements $[(W_2O_9)^{6-}]\infty$ in the structure of new obtained compounds. The products of a reaction between $ZnWO_4$ and RE_2MoO_6 (*RE*=Y, Ho, Er, Lu) are: ZnO, an adequate rare-earth metal tungstate RE_2WO_6 and an adequate rare-earth metal molybdate $RE_2(MoO_4)_3$.

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