Studies on reactivity in the solid state between some rare-earth metal oxides Ln_2O_3 where Ln=Y, La, Nd, Sm, Eu, Gd, Dy, Ho, Er, Lu and metal sulfates(VI) MSO_4 where M=Ni, Cu, Zn, Cd

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Chemistry of lanthanides has become of great importance over several decades because of its use in numerous applications. Rare-earth oxysulfates(VI) are the subject of considerable interest because of their specific luminescent properties and practical using in the color cathode-ray tubes [1, 2]. The rare-earth elements form the family of oxysulfate(VI) compounds with the formula $(LnO)_2SO_4$ [3–9]. These compounds are usually synthesized, as intermediate products, by thermal decomposition of the corresponding anhydrous sulfates(VI) [3, 4] or by oxidation of the corresponding oxysulfides Ln_2O_2S [4–7]. The specific heat and magnetic susceptibility measurements have shown that $(LnO)_2SO_4$ are anti-ferromagnetics with the transition temperature range from 0.6 to 30 K [8]. The rare-earth oxysulfates(VI) decompose to the corresponding rare-earth oxide [5]. The stability of oxysulfates(VI) and their decomposition temperatures decrease with decreasing radius of the rare-earth ion [5]. Haynes and Brown [1] were the first to determine the lattice constants of $(GdO)_2SO_4$. This phase crystallizes in the orthorhombic system and has the following parameters of the unit cell: a=4.062, b=4.188, c=12.96 Å [1]. Laptev *et al.* [9] found that $(LnO)_2SO_4$ where Ln=Y, La, Pr, Nd, Sm–Tb crystallize in the orthorhombic system with the lattice constants: a=4.2647 (for La)÷4.11 (for Tb) Å; b=4.165 (for La)÷3.967 (for Tb) Å; c=13.7103 (for La)÷12.74 (for Tb) Å. The structure of lanthanum oxysulfate(VI) $(LaO)_2SO_4$ was studied with neutron, electron, and X-ray diffraction using the Rietveld refinement method by Zhukov *et al.* [10]. The authors suggest that $(LaO)_2SO_4$ was monoclinic with the following lattice constants: a=14.349(1), b=4.2852(5), c=8.386(1) Å, space group—$C2/c$ [10]. The structure of $(LaO)_2SO_4$ is similar to that of the grandreefite ($Pb_2F_2SO_4$) and consists of alternative sulfate(VI) and (LaO) layers. Every sulfate(VI) oxygen atom is coordinated with two lanthanum atoms [10].

This paper presents the results of investigations concerning reactivity in the solid state between some rare-earth metal oxides Ln_2O_3 and selected sulfates(VI) of d-electron metals. New basic crystallographic parameters, IR spectra and thermal properties of $(LnO)_2SO_4$ (Ln=Y, La, Nd, Sm–Gd, Dy–Er) are given, too.

Analytical-grade Y_2O_3 (cubic, 99.9%), Nd_2O_3 (hexagonal, 99.9%), Eu_2O_3 (cubic, 99.9%), Gd_2O_3 (cubic, 99.9%), Dy_2O_3 (cubic, 99.9%), Ho_2O_3 (cubic, 99.9%), Er_2O_3 (cubic, 99.9%) and Lu_2O_3 (cubic, 99.9%) were used as starting materials. By adding an excess of aqueous solution of oxalic acid to dissolved nitrates(V) of La and Sm, the oxalates of the corresponding metals were precipitated. The oxalates were converted into the oxides La_2O_3 (hexagonal) and Sm_2O_3 (a mixture of cubic and monoclinic modifications) by heating at 850 °C for 2×8 hr. Before experiments all oxides were preliminary heated at 850 °C for a 30-h period to eliminate traces amounts of water and CO_2. Anhydrous metal sulfates(VI) were obtained by heating: $NiSO_4{\cdot}6H_2O$, $CuSO_4{\cdot}5H_2O$, $ZnSO_4{\cdot}7H_2O$ and $3CdSO_4{\cdot}8H_2O$ at 550 °C for 12 hr. Equimolar mixtures of anhydrous MSO_4 and corresponding rare-earth metal oxide were heated in air, in the following cycles: 600 °C (24 hr), 650 °C (24 hr), 700 °C (24 hr), 750 °C (24 hr), 770 °C (3×24 hr). After each heating cycle all samples were gradually cooled to ambient temperature, weighed, ground and examined for their contents by XRD method and afterwards heated until an equilibrium state had been established. If after at least two successive stages of heating the XRD results were identical an equilibrium was considered. Mass changes (decreases) of samples were observed during heating only Lu_2O_3/MSO_4 mixtures.

All samples obtained after the final heating cycle of Ln_2O_3/MSO_4 mixtures were subjected to examination by DTA/TG methods in a nitrogen atmosphere.

To determine the solid products of decomposition all the samples in an equilibrium state were heated in air, at 1300 °C, for 3 hr. After heating time the samples were cooled to ambient temperature, weighed and examined by XRD and IR methods.

X-ray diffraction phase analysis of the samples was performed by a diffractometer DRON-3 using $CoK_{\alpha\ \mathrm{aver.}}$ radiation (λ=1.70921 Å).

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TABLE I Results of XRD analysis of samples obtained after final heating cycle of Ln_2O_3/MSO_4 mixtures

	Ln_2O_3 Ln=Y, La, Nd, Sm, Eu, Gd, Dy, Ho, Er	Lu_2O_3
$NiSO_4$	$(LnO)_2SO_4$, NiO (cubic)	Lu_2O_3, $NiSO_4$, NiO (traces)
$CuSO_4$	$(LnO)_2SO_4$, CuO (monoclinic)	Lu_2O_3, Cu_2OSO_4, CuO (monoclinic)
$ZnSO_4$	$(LnO)_2SO_4$, ZnO (hexagonal)	Lu_2O_3, $Zn_3O(SO_4)_2$
$CdSO_4$	$(LnO)_2SO_4$, CdO (cubic)	Lu_2O_3, $CdSO_4$ (orthorhombic)

The DTA-TG examinations were performed using a TA Instruments SDT 2960 apparatus. These measurements were carried out within temperature range of 20–1500 °C, in a nitrogen atmosphere, using corundum crucibles and at the heating rate of 10 K/min.

The IR spectra were recorded on a Specord M-80 spectrometer (Carl Zeiss Jena). The samples were pressed in pellets with KBr.

Table I shows results of XRD analysis for samples obtained after the final heating stage of equimolar Ln_2O_3/MSO_4 mixtures. The data of the table indicate that initial components of Ln_2O_3/MSO_4 mixtures, where Ln=Y, La, Nd, Sm, Eu, Gd, Dy, Ho, Er and M=Ni, Cu, Zn, Cd, reacted in air. On each of powder diffraction patterns of samples in equilibrium state two sets of diffraction lines were identified. One of each two sets characterized the corresponding metal oxide MO. The other set of diffraction lines for samples obtained after heating Ln_2O_3/MSO_4 mixtures (Ln=Y, La, Nd, Sm, Eu and Gd) comprised reflexions whose number and angle position were different compared to the position of diffraction lines published in case of $(LnO)_2SO_4$ compounds (Ln=Y, La–Gd) [9]. As to the samples, the initial mixtures of which contained Ln_2O_3 (Ln=Dy–Er) with MSO_4, this set of diffraction line could not be attributed to any of the compounds occurring in Ln–S–O ternary systems. No information was found in current literature about existence of $(LnO)_2SO_4$ compounds where Ln=Dy–Er. On the other hand, XRD analysis of the samples obtained after the final heating stage of Lu_2O_3/MSO_4 (M=Ni, Cu and Zn) mixtures has shown that they were a mixture of Lu_2O_3 and intermediate or final products of thermal decomposition of an appropriate MSO_4. However, a powder diffraction pattern of a sample in an equilibrium state, the initial mixture of which comprised Lu_2O_3 and $CdSO_4$ showed only reflexions considered to be characteristic for initial components this mixture.

Based on the experimental results obtained using XRD method and considering that during heating Ln_2O_3/MSO_4 mixtures (Ln=Y, Sm, Eu, Gd, Dy, Ho and Er) no mass changes of samples could be found, one can state that the reaction of chosen rare earths with some sulfates(VI) of d-electron metals can be described by the following reaction:

$$Ln_2O_{3(S)} + MSO_{4(S)} = (LnO)_2SO_4(S) + MO_{(S)} \tag{1}$$

Powder diffraction patterns of samples obtained after the final heating stage were applied to indexing of $(LnO)_2SO_4$ phases. A total of 15 or 16 successive diffraction lines (not being the lines of the set characterizing MO) were selected for indexing by POWDER program [11, 12]. Table II shows the results of indexing powder diffraction patterns. The parameters of $(LnO)_2SO_4$ unit cells have been tabulated in Table III. It follows from the data shown in Tables II and III that the obtained compounds crystallize in the orthorhombic system and they are isostructural. As the radius of Ln^{3+} ion is decreasing, the parameters of $(LnO)_2SO_4$ unit cells decrease, too.

Fig. 1 shows IR spectra of samples obtained after the final heating cycle of $Ln_2O_3/NiSO_4$ equimolar mixtures. For comparative purposes, IR spectrum of Gd_2O_3 as well as spectrum of anhydrous $NiSO_4$ are showed

TABLE II Results of indexing $(LnO)_2SO_4$ powder diffraction patterns

	$(YO)_2SO_4$		$(LaO)_2SO_4$		$(NdO)_2SO_4$		$(SmO)_2SO_4$		$(EuO)_2SO_4$		$(GdO)_2SO_4$		$(DyO)_2SO_4$		$(HoO)_2SO_4$		$(ErO)_2SO_4$		
No.	d (Å)	I/I_0	d (Å)	I/I_0	d (Å)	I/I_0	d (Å)	I/I_0	d (Å)	I/I_0	d (Å)	I/I_0	d (Å)	I/I_0	d(Å)	I/I_0	d (Å)	I/I_0	h k l
1	6.3481	14	6.8569	13	6.6712	15	6.5612	16	6.5158	14	6.4832	26	6.3833	27	6.3566	23	6.3178	24	0 0 2
2	3.9399	7	4.0868	14	4.0274	14	4.0013	13	3.9862	10	3.9741	13	3.9444	15	3.9360	14	3.9257	12	0 1 1
3	3.8269	5	4.0120	12	3.9326	12	3.8948	10	3.8847	8	3.8690	11	3.8367	12	3.8218	12	3.8066	10	1 0 1
4	2.9608	100	3.1246	96	3.0620	100	3.0292	100	3.0147	100	3.0038	100	2.9714	100	2.9619	100	2.9498	100	0 1 3
5	2.9127	84	3.0912	100	3.0207	94	2.9862	92	2.9706	95	2.9575	94	2.9246	93	2.9123	92	2.8990	90	1 0 3
6	2.8831	94	2.9964	87	2.9486	92	2.9278	94	2.9182	96	2.9088	91	2.8885	97	2.8796	96	2.8720	96	1 1 0
7			2.7456	14			2.6739	10	2.6635	7	2.6544	8	2.6320	10	2.6228	10	2.6121	12	1 1 2
8	2.1644	13	2.3096	12	2.2545	13	2.2253	13	2.2135	12	2.2035	11	2.1762	12	2.1680	13	2.1564	13	0 1 5
9	2.1451	16	2.2944	17	2.2382	15	2.2095	16	2.1953	15	2.1859	12	2.1570	15	2.1478	17	2.1356	12	1 0 5
10	2.1350	16	2.2864	20	2.2231	21	2.1863	32	2.1736	33	2.1644	28	2.1426	16	2.1348	17	2.1268	13	1 1 4
11	2.1162	16	2.2568	23	2.2087	22							2.1293	16	2.1200	17	2.1070	16	0 0 6
12	2.0721	20	2.1418	18	2.1126	20	2.0997	22	2.0943	16	2.0881	14	2.0755	18	2.0712	19	2.0660	16	0 2 0
13	2.0069	26	2.0978	28	2.0590	25	2.0431	22	2.0358	24	2.0279	20	2.0129	20	2.0047	22	1.9973	16	2 0 0
14	1.9704	15	2.0435	11	2.0136	14	1.9999	14	1.9940	13	1.9884	10	1.9741	11	1.9693	12	1.9636	10	0 2 2
15	1.9133	8	2.0062	9	1.9674	10	1.9501	9	1.9428	8	1.9354	7	1.9196	8	1.9116	8	1.9051	5	2 0 2
16	1.8218	5	1.8897	5	1.8613	6	1.8484	6	1.8426	6	1.8380	4	1.8263	5	1.8206	6	1.8152	5	1 2 1

TABLE III Calculated parameters of the unit cells for $(LnO)_2SO_4$

	a (Å)	b (Å)	c (Å)	b/a	c/a
$(YO)_2SO_4$	4.0136(3)	4.1448(2)	12.694(8)	1.0327	3.1629
$(LaO)_2SO_4$	4.1955(4)	4.2829(6)	13.715(1)	1.0208	3.2690
$(NdO)_2SO_4$	4.1178(6)	4.2248(6)	13.334(6)	1.0260	3.2382
$(SmO)_2SO_4$	4.0851(3)	4.1989(7)	13.129(8)	1.0279	3.2140
$(EuO)_2SO_4$	4.0707(2)	4.1875(8)	13.034(1)	1.0287	3.2019
$(GdO)_2SO_4$	4.0553(5)	4.1767(6)	12.969(4)	1.0299	3.1981
$(DyO)_2SO_4$	4.0251(4)	4.1512(2)	12.774(6)	1.0313	3.1737
$(HoO)_2SO_4$	4.0084(9)	4.1414(9)	12.719(4)	1.0332	3.1731
$(ErO)_2SO_4$	3.9948(3)	4.1309(8)	12.641(3)	1.0341	3.1644

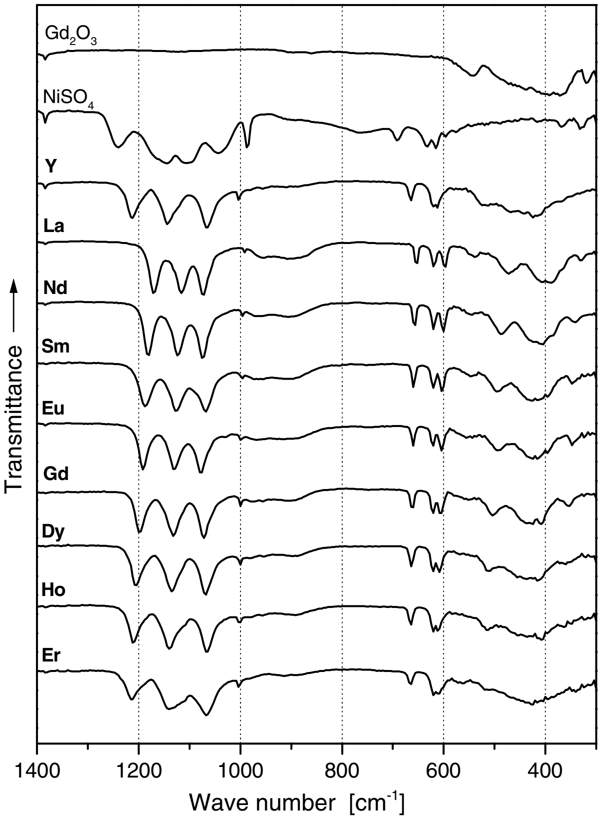

Figure 1 IR spectra of samples obtained after the final heating cycle of $Ln_2O_3/NiSO_4$ mixtures.

in Fig. 1, too. In the light of the published information [13–17] the absorption bands recorded in $NiSO_4$ spectrum and showing their maxima in the wave number range of 1300–1000 cm^{-1} are ascribed to stretching vibrations of S–O bonds in SO_4 tetrahedra. Next, absorption bands with maxima in the range 700–600 cm^{-1} can be due to the stretching vibrations of O–S–O in SO_4 tetrahedra [13–17]. Absorption bands with their maxima lower than 600 cm^{-1} can be attributed to Ni–O bonds in NiO_6 octahedra [18]. In IR spectrum of Gd_2O_3 the maxima of absorption bands were recorded only below 600 cm^{-1}. Those bands are assigned for the stretching modes of Gd–O bonds in GdO_6 octahedra [19]. As it is evident from Fig. 1 IR spectra of all the samples obtained on the final heating cycle of $Ln_2O_3/NiSO_4$ mixtures are similar each with respect to the number and intensity of absorption bands recorded within the wave number ranges, i.e. from 1200 to 1000 cm^{-1} and from 700 to 600 cm^{-1}. According to the literature information [13–17], absorption bands with their maxima lying at the wave number range of ∼1200÷1000 cm^{-1} can be ascribed to the stretching vibrations of S–O bonds in SO_4 tetrahedra. Absorption bands of this wave number range were observed in vibrational spectra of solid sulfates(VI) comprising a sulfur atom in tetrahedral surrounding [13–17]. On the other hand, absorption bands showing maxima at the latter wave number range under consideration can be assigned to the stretching vibrations of O–S–O bonds in SO_4 tetrahedra [13–17]. A distinct splitting of absorption bands responsible for the stretching vibrations of S—O and O—S—O bonds is indicative of considerable deformation of SO_4 tetrahedra. Furthermore, one can observe a slight shift of maxima absorption band towards higher wave numbers when the radius of Ln^{3+} ion is decreasing. The similarities among IR spectra of samples in an equilibrium state give a clear indication that the $(LnO)_2SO_4$ compounds arising from the reaction (1) are isostructural. IR spectra of samples in an equilibrium state (Fig. 1) show also a number of absorption bands with their maxima recorded below 600 cm^{-1}. The bands can be attributed to the stretching vibrations of Ni—O bonds in NiO_6 octahedra occurring in NiO and Ln—O in LnO_6 octahedra which occur in Ln_2O_3 as well as to the stretching vibrations of Ln—O in LnO_x polyhedra existing in $(LnO)_2SO_4$ structures. Fig. 2 shows

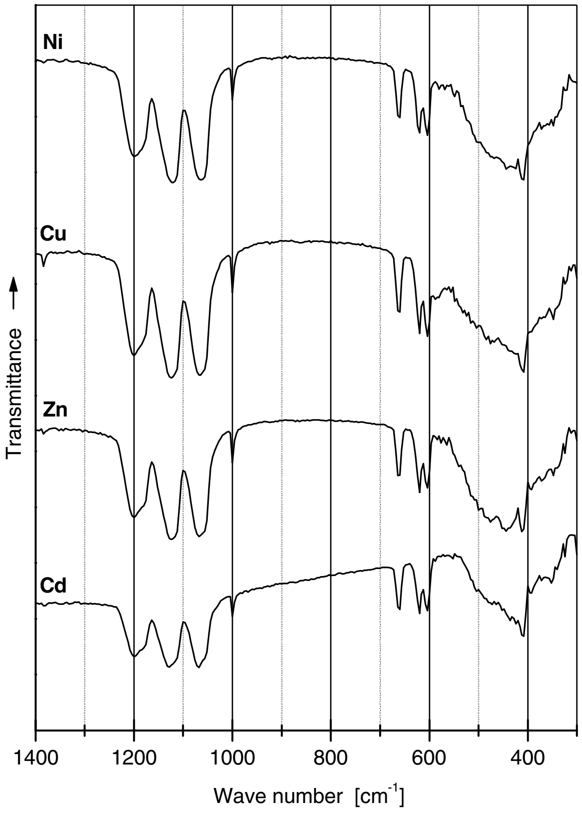

Figure 2 IR spectra of samples obtained after the last heating cycle of Gd_2O_3/MSO_4 mixtures.

TABLE IV Values of onsets of first endothermic effects recorded on DTA curves of samples in an equilibrium state

	Temperature (°C)			
	$NiSO_4$	$CuSO_4$	$ZnSO_4$	$CdSO_4$
Y	976	978	984	971
La	1079	1085	1094	1081
Nd	1047	1052	1059	1038
Sm	1022	1029	1034	1013
Eu	1002	993	1006	988
Gd	986	984	999	973
Dy	975	979	983	969
Ho	964	964	971	952
Er	935	931	946	928

IR spectra of samples in an equilibrium state obtained after heating mixtures of Gd_2O_3 with MSO_4 (M=Ni, Cu, Zn and Cd). A striking similarity among IR spectra at the wave number range of $\sim 1200 \div 1000$ cm^{-1} and $\sim 700 \div 600$ cm^{-1} gives an indication that one of the products of reaction between Gd_2O_3 and MSO_4 is $(GdO)_2SO_4$, regardless the sulfate(VI) of a divalent metal employed in the reaction.

On each DTA curves of the samples in an equilibrium state only endothermic effects were recorded, the number of which (1, 2, or 3) was dependent on used reagents. It has been observed that onsets of first effect recorded on DTA curves are similar to each other when samples are obtained by heating $(LnO)_2SO_4/MO$ mixtures, where Ln—the given rare-earth metal and M—any divalent metal. Their values have been tabulated in Table IV. First endothermic effects are accompanied by mass decrements starting at the same temperature (Fig. 3, TG curves of $(LnO)_2SO_4/CdO$ mixtures). Table V shows results of XRD analysis samples obtained after heating $(LnO)_2SO_4/MO$ mixtures in 1300 °C for 3 hr. The data presented in the Table V show that $(LnO)_2SO_4$ compounds undergo thermal decomposition in the solid state to the corresponding rare-earth oxide. It was found that two solid phases, i.e. Ln_2O_3 and ZnO occurred in the samples comprising initially $(LnO)_2SO_4/ZnO$ mixtures on treatment. Total thermal decomposition of $(LaO)_2SO_4$ was not achieved for a sample comprising initially $(LaO)_2SO_4/ZnO$ mixture. XRD analysis of preparations obtained after decompositions of samples obtained on heating mixtures comprising initially $(LnO)_2SO_4/CdO$ showed that they contained only Ln_2O_3 (CdO undergoes sublimation above 1000 °C). A sample, the initial mixture of which comprised $(LaO)_2SO_4$ and CdO, contained $(LaO)_2SO_4$ and $La(OH)_3$ (lanthanum hydroxide is formed by immediate moisture absorption by La_2O_3 from air whenever the sample is taken from furnace). Preparations obtained on heating at 1300 °C for 3 hr of samples the initial mixtures of which comprised $(LnO)_2SO_4$ and CuO contained:

– Ln_2O_3 and $Ln_2Cu_2O_5$ [20–25] (products of reaction between Ln_2O_3 and CuO) where Ln=Y, Dy, Ho, and Er

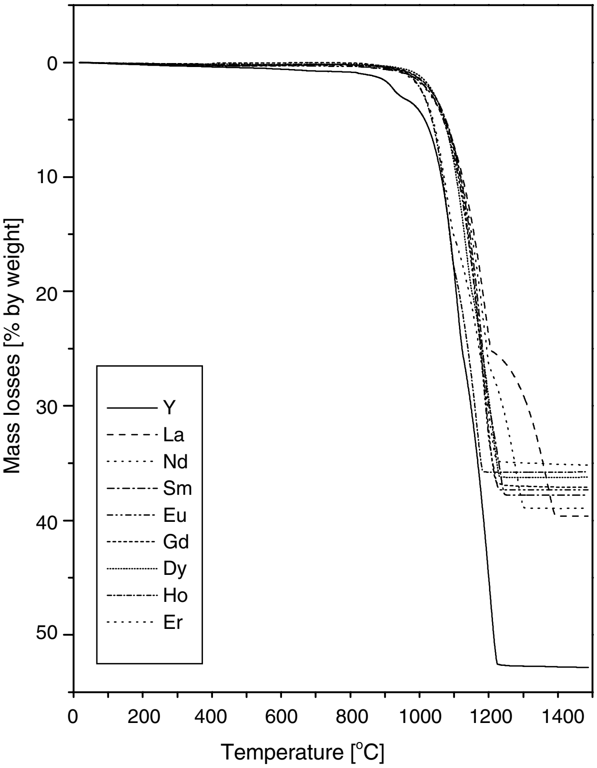

Figure 3 TG curves of samples obtained after the last heating cycle of $Ln_2O_3/CdSO_4$ mixtures.

– $(LnO)_2$ SO_4 and Ln_xCuO_y x=1.83–2, y=3.84–4.25 [21, 22, 26, 27] (products of reaction of Ln_2O_3 CuO) where Ln=La, Nd, Sm, Eu and Gd.

XRD analysis of preparations obtained after thermal decomposition at 1300 °C of samples obtained on heating mixtures comprising initially $(LnO)_2SO_4/NiO$ has shown that they contained Ln_2O_3 and NiO, where Ln=Y, Sm, Eu, Gd, Dy, Ho and Er. It was found that only the sample after decomposition, prepared with La_2O_3, contained a mixture of La_xNiO_y, x=1.83–2, y=3.84–4.25 [28–30] and an incompletely decomposed $(LaO)_2SO_4$. Unlike the above discussed compounds a preparation obtained after thermal decomposition at 1300 °C of a sample comprising $(NdO)_2SO_4/NiO$ contained only Nd_2NiO_y y=4 or 4.199 [31].

Fig. 4 shows IR spectra of samples obtained after thermal decomposition of preparations in an equilibrium state, the initial mixtures of which comprised Gd_2O_3 and MSO_4 (spectra c). For the comparison purpose, IR spectra of Gd_2O_3 (spectra a) and initial preparations subjected to decomposition at 1300 °C (spectra b) are shown, too. In IR spectra of samples after decomposition, lack of absorption bands assigned for the stretching vibrations of S—O and S—O—S bonds in SO_4 tetrahedra clearly indicates that thermal decomposition of $(LnO)_2SO_4$ runs with liberation of SO_2.

TABLE V Results of XRD analysis performed for samples obtained after decomposition at 1300 °C for 3 hr and experimental as well as observed mass losses

	$NiSO_4$	$CuSO_4$	$ZnSO_4$	$CdSO_4$
Y	Y_2O_3 (cubic), NiO	Y_2O_3 (cubic), $Y_2Cu_2O_5$	Y_2O_3 (cubic), ZnO	Y_2O_3 (cubic)
La	$(LaO)_2SO_4$, La_xNiO_y $\substack{x=1.83\div2 \\ y=3.84\div4.25}$	$(LaO)_2SO_4$, La_xCuO_y $\substack{x=1.83\div2 \\ y=3.84\div4.25}$	$(LaO)_2SO_4$, ZnO,* $La(OH)_3$	$(LaO)_2SO_4$,* $La(OH)_3$
Nd	$Nd_2NiO_{yy=4or4.199}$	$(NdO)_2SO_4$, Nd_xCuO_y $\substack{x=1.972\div2 \\ y=3.88\div4.178}$	Nd_2O_3 (hexagonal), ZnO, $(NdO)_2SO_4$	Nd_2O_3 (hexagonal)
Sm	Sm_2O_3 (monoclinic), NiO	$(SmO)_2SO_4$, Sm_2CuO_4	Sm_2O_3 (monoclinic), ZnO	Sm_2O_3 (monoclinic)
Eu	Eu_2O_3 (monoclinic), NiO	$(EuO)_2SO_4$, Eu_2CuO_4, Eu_2O_3 (monoclinic)	Eu_2O_3 (monoclinic), ZnO	Eu_2O_3 (monoclinic)
Gd	Gd_2O_3 (monoclinic), Gd_2O_3 (cubic), NiO	Gd_2O_3 (monoclinic) Gd_2CuO_x x=3.98 or 4.00	Gd_2O_3 (monoclinic), ZnO	Gd_2O_3 (monoclinic), Gd_2O_3 (cubic)
Dy	Dy_2O_3 (cubic), NiO	Dy_2O_3 (cubic), $Dy_2Cu_2O_5$	Dy_2O_3 (cubic), ZnO	Dy_2O_3 (cubic)
Ho	Ho_2O_3 (cubic), NiO	Ho_2O_3 (cubic), $Ho_2Cu_2O_5$	Ho_2O_3 (cubic), ZnO	Ho_2O_3 (cubic)
Er	Er_2O_3 (cubic), NiO	Er_2O_3 (cubic), $Er_2Cu_2O_5$	Er_2O_3 (cubic), ZnO	Er_2O_3 (cubic)

*$La(OH)_3$ is formed by immediate moisture absorption by La_2O_3 from air

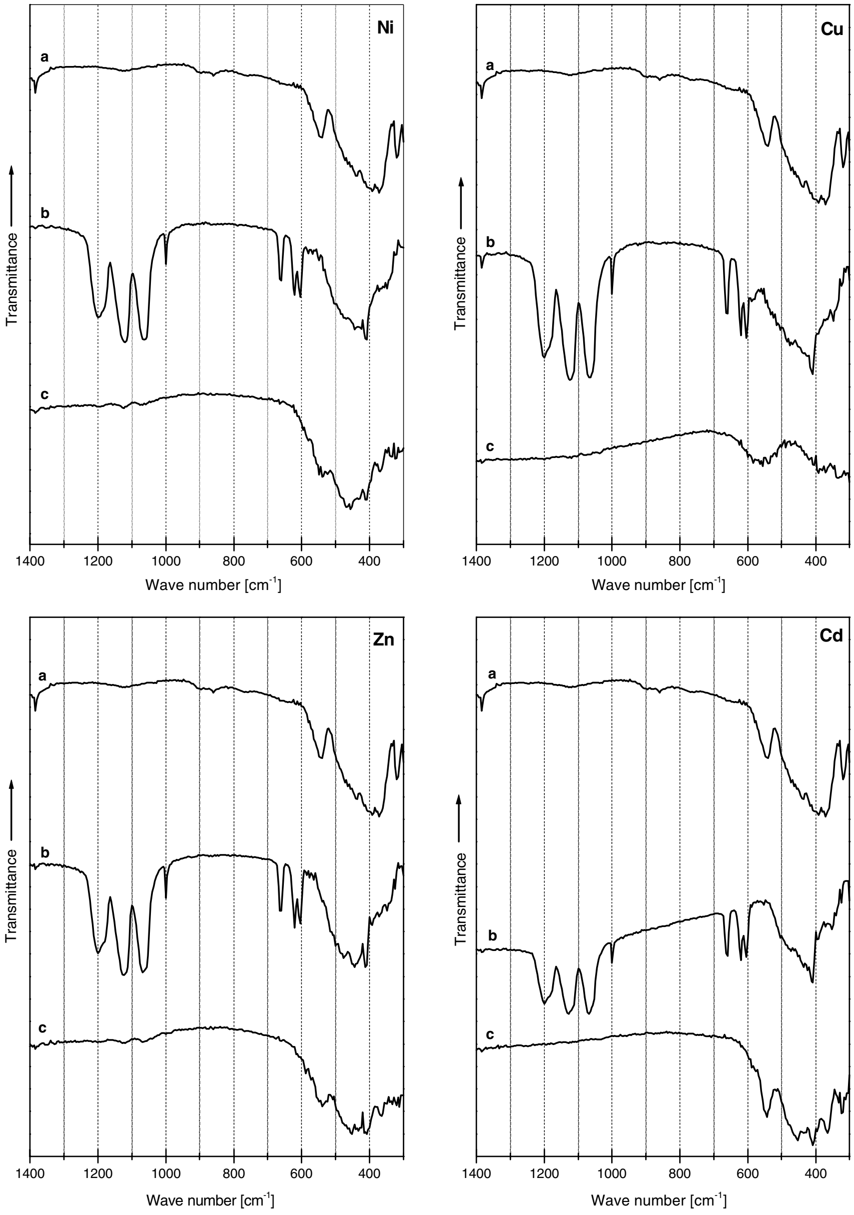

Figure 4 IR spectra for: a—Gd_2O_3; b—samples obtained after the last heating cycle of Gd_2O_3/MSO_4 mixtures; c–samples obtained after thermal decomposition.

The experimental results concerning reactivity of selected rare-earths with sulfates(VI) of divalent metals have led to the following conclusions:

– $(LnO)_2SO_4$ compounds are formed not only in effect of thermal decomposition of $Ln_2(SO_4)_3$ or oxidation of Ln_2O_2S but also in a reaction taking lace in the solid state between rare-earth metal oxides Ln_2O_3 (Ln=Y, La, Nd, Sm, Eu, Gd, Dy, Ho and Er) and sulfates(VI) of d-electron metals MSO_4 (M=Ni, Cu, Zn and Cd). The other product of this reaction is the corresponding metal oxide MO,

– reaction of Lu_2O_3 with MSO_4 does not lead to $(LuO)_2SO_4$,

– $(LnO)_2SO_4$ are isostructural compounds and crystallize in the ortorhombic system,

– oxysulfates(VI) of rare-earth metals undergo thermal decomposition to the corresponding Ln_2O_3,

– thermal stability of $(LnO)_2SO_4$ is decreasing from La to Er.

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