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Mechanochemical synthesis of some europium diketonates

Research Article

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Abstract: Results on the influence of mechanoactivation (3-30 min) in a planetary ball mill on the composition, crystal structure, IR spectra and morphology of EuCl3•6H2O, dibenzoylmethane (HDBM) and mixtures of $EuCl_3•6H_2O$ - HDBM and $EuCl_3•6H_2O$ - HDBM – 1,10-phenathroline (phen) are presented. Mechanoactivation leads to a decrease of interplanar distances of the $EuCl_3•6H_2O$ and HDBM and partial synthesis of $Eu(DBM)_3$ and $Eu(DBM)_3•phen$ in the respective mixtures. The fluorescence properties of the products of activation (excitation and emission spectra, lifetime of the excited states) are similar to those of the complexes produced by the conventional "wet" methods, but the strongest excitation of the mechanochemically produced solid state samples is achieved at higher wavelength. Crystals of different forms (prismatic, needle-, long-length-leaf- and rod- like) are formed by mechanoactivation of the mentioned mixtures.

Keywords: *Mechanochemistry • Europium complexes • XRD • SEM • Photoluminescence*

1. Introduction

Recently, the chemistry and application of lanthanide β-diketonates have been the subject of excellent reviews [1-3]. The chemical and thermal instability of the complexes create complications for their synthesis; some peculiarities of the lanthanide dibenzoylmethanate wet synthesis have been discussed in [4]. Mechanical activation is a well known self-dependant method or important supplement to the conventional methods for preparation of a number of chemical substances. However, there are rather few investigations on the mechanochemical synthesis of lanthanoid complexes. Successful synthesis of compounds of the type $Ln(NO_3)_3•2D$ (Ln = Eu or Tb, D=2,2-dipyridyl, 1,10-phenanthroline, diphenylguanidine) is reported in [5]. The activation has been performed in an AGO-2 centrifugal-planetary ball mill for 5-10 min at 1000 min^{-1} and room temperature in air or as suspension in water or ethanol. The activated products have been washed with water-ethanol mixture. The authors claimed that the luminescence intensity of the materials produced is equal to the ones obtained by traditional methods. The development of the IR spectral characteristics and morphology of a mixture of $Eu(NO_3)_3$ and 1,10-phenanthroline with the progress of mechanoactivation is studied in more details in [6]. Mechanochemical synthesis of $EuDik_3•nH_2O$ particles, 10-300 μm in size (Dik = dibenzoylmethane, n = 1; benzoylacetone, benzoyltrifluoracetone, n = 3) is described in [7], with the maximum yield reached after 2.5-3 min. The effect of the mechanical treatment conditions and of the nature of the initial products on the synthesis of mixed-ligand Eu complexes of the type $EuDik_3•D$, where Dik = dibenzoylmethane, benzoylacetone, thenoyltrifluoracetone, benzoyltrifluoracetone; D = 2,2-dipyridyl, 1,10-phenanthroline, diphenylguanidine, is reported in [8]. The morphology and particle size distribution is further studied in [9].

In the present paper, the influence of mechanoactivation on the initial substances $EuCl_3•6H_2O$ and dibenzoylmethane (HDBM) and the results of mechanochemical interaction in the systems $EuCl_3•6H_2O$-HDBM and $EuCl_3•6H_2O$-HDBM-1,10-phenanthroline at longer activation time are studied in more detail. The changes in X-ray diffractograms, IR spectra, morphology and photoluminescence properties of the reaction products are followed.

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2. Experimental Procedure

2.1. Materials

HDBM (purum, >98%, supplied by Fluka), 1,10-phenanthroline (phen, 99%, Alfa Aesar), $EuCl_3 \cdot 6H_2O$, (99%, Fluka) and NaOH (p.a.) were used as starting materials for complex production.

2.2. Complex synthesis

5 g of pure starting product or mixtures of the respective ligand(s) and complexing agents in the desired molar ratio with 0.02 g NaOH were subjected to mechanoactivation for 3 - 30 min at 800 min^{-1} in a Pulverisette 7 planetary ball mill. The 45 mL zirconia vessels were filled to 2/3 of the volume with balls of 5 (mainly) and 10 mm in diameter of the same material. The milled material was treated under stirring in excess of a 1:1 ethanol - water mixture [7] for 6 h to dissolve the unreacted initial products. The residue was filtered and dried at 40°C.

The obtained products were compared with $Eu(DBM)_3$ and $Eu(DBM)_3$•phen prepared by the methods proposed in [10,11] and applied in [4].

2.3. Analysis and characterization

The content of H, C, and N (the latter in the complexes containing 1,10-phenanthroline) were determined by means of a Vario EL III V5.018 elemental analyzer.

The IR spectra were recorded by a Bruker spectrometer in KBr pellets. The X-ray diffractograms were taken by a Siemens D500 powder diffractometer at CuK_α, 40 kV, 2θ step 0.02°/2 s.

The morphology was studied by fluorescence (N-400M microscope) and scanning electron (Jeol JSN 5510) microscopy. The absorption and emission photoluminescence spectra and the lifetime of the excited states were recorded using a Cary Eclipse fluorescence spectrometer (Varian) in 10^{-5} M dimethylformamid (DMF) solution or in the solid state.

3. Results and Discussion

3.1. X-ray diffraction data

X-ray diffractograms of the initial materials and of the products of mechanoactivation are shown in Figs. 1, 2.

Mechanoactivation causes significant amorphisation of the $EuCl_3 \cdot 6H_2O$ (Fig. 1), progressing with activation time. The effect is much weaker in the case of HDBM (Fig. 2). The interplanar distances decrease on average by 1.3% for $EuCl_3 \cdot 6H_2O$ and by 0.7% for HDBM for the 30 min-activated samples compared with the initial products.

The progress of the synthesis of $Eu(DBM)_3$ from the $EuCl_3 \cdot 6H_2O$ – HDBM mixture by mechano-activation, together with the activated individual components are shown in Fig. 3. The relative intensity of the 3.63 Å reflection of HDBM (the strongest one in the mechanoactivated HDBM diffractogram) decreases to 31% and to 14% after 3 and 30 min activation of the reaction mixture, respectively. The relative intensities of the reflections of $Eu(DBM)_3$ around 11.4, 5.70, 4.85 and 3.64 Å, which can be considered as practically free from influences of the initial reagents, increase with the activation time from 60, 21, 24, 31% (3 min) to 100, 30, 57, 42% (30 min), respectively. The intensities of the reflections at 12.11, 5.22 and 4.54 Å, which are the result of superposition of initial compounds and the final product of their interaction, also increase with activation time. However, the X-ray diffraction data show that the $Eu(DBM)_3$ produced by the applied procedure contains unreacted HDBM and some chloride as well. The results from the elemental analysis (Table 1) confirm this observation, suggesting that the composition of the product obtained after 30 min of activation can be described as $Eu(DBM)_3$ + 0.5HDBM.

When discussing the polyphase character of the mechanochemically obtained product, one has to consider not only the incompleteness of the reaction between the starting products but also the possible destruction of the produced complex. Its thermal instability is mentioned in number of publications (see for example reference [4] and the papers cited in it). The well known local increase of the temperature during high-energy mechanical treatment may cause a decomposition of the formed complex, leading to some kind of mechanochemical equilibrium. Such equilibrium has been observed between the formation and destruction of solid solutions in the course of mechanoactivation of individual lanthanoid oxides [12]. However, according to literature data, the formation of polynuclear europium clusters [1,2] seems much more likely to be a result of heating and dehydration of the complexes occurring during some mechanochemical processes.

The results obtained for the system $EuCl_3 \cdot 6H_2O$-HDBM-phen compared with $Eu(DBM)_3$•phen produced by "wet" methods are shown in Fig. 4. Despite the similarity in the diffractograms, the presence of both unreacted HDBM and phen is seen along with significant shifts of some of the complex reflections. The elemental analysis (Table 1) suggests that the tentative formula of the activated product is $Eu(DBM)_3 \cdot phen \cdot nH_2O$ + 3(HDBM+phen). The presence of H_2O is confirmed by the IR spectrum and the thermogravimetric analysis results discussed below.

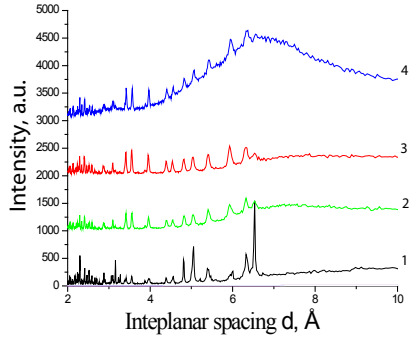

Figure 1. X-ray diffractograms of $EuCl_3 \cdot 6H_2O$ before (1) and after 3 (2), 10 (3) and 30 (4) min activation.

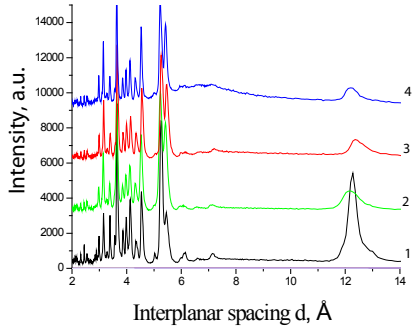

Figure 2. X-ray diffractograms of HDBM before (1) and after 3 (2), 10 (3) and 30 (4) min activation.

The crystallite sizes calculated from the broadening of the 6.33/6.26 Å reflections for $EuCl_3 \cdot 6H_2O$, 3.65/3.63 Å for HDBM, 11.33 Å for the complex $Eu(DBM)_3$ and 10.53 Å for the complex $Eu(DBM)_3 \cdot$phen is shown in Table 2. Here, the influence of the mechanoactivation is rather different for the different samples. It leads to a significant decrease of the $EuCl_3$ crystallite size (in comparison with non-activated samples) with a minimum at 10 min of activation, a weak decrease for HDBM with a recovery of the size after 30 min activation time. Crystallites of the formed $Eu(DBM)_3$ are larger than the ones of the product prepared by the conventional method. The opposite effect is seen for $Eu(DBM)_3 \cdot$phen.

3.2. IR spectral data

IR spectra of the mechanoactivated individual products and $EuCl_3.H_2O$ – HDBM mixture are presented in Fig. 5. They were interpreted according to [4,13]. The spectra confirm the polyphase composition of the activated samples. It is seen that the complexation moves some of the HDBM bands towards lower wave numbers: bands at 1541 cm^{-1} and 1600 cm^{-1} ascribed to ν_{as}(C=C) and to ν_{as}(C=O) in HDBM appear at 1524-1528 cm^{-1} and 1597 cm^{-1} in the 30 min-activated sample; the bands of π(CH) move from 924/758 cm^{-1} to 940/755 cm^{-1} in the

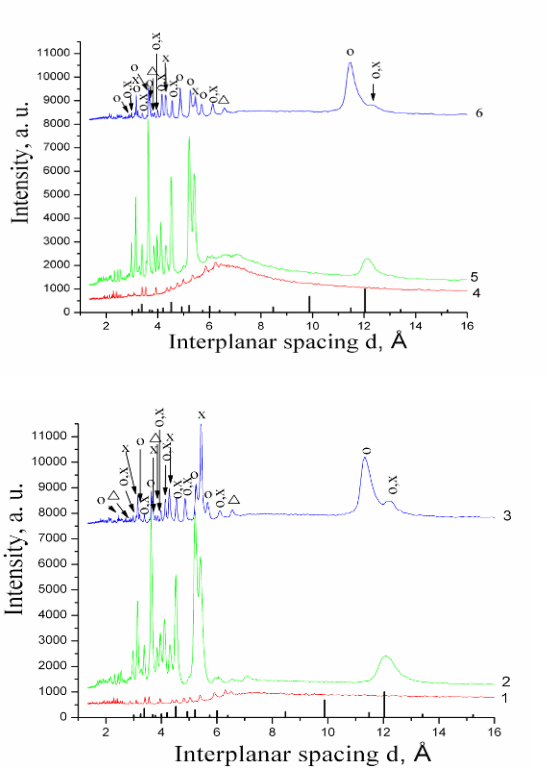

Figure 3. X-ray diffractograms of $EuCl_3 \cdot H_2O$ (1, 4), HDBM (2, 5) and $EuCl_3 \cdot H_2O$ – HDBM mixture (3, 6) after 3 (1-3) and 30 (4-6) min mechanoactivation: o - $Eu(DBM)_3$, x – HDBM, Δ - $EuCl_3 \cdot 6H_2O$. Positions of reflexes in wet chemistry-produced complex are shown on the abscissa.

Table 1. Content of H, C and N (%) in HDBM and in some of the complexes.

Sample	H	C	N
HDBM	5.39	80.33	
$Eu(DBM)_3$*	4.02	65.80	
$Eu(DBM)_3$, mechano-activated, 3 min	4.89	75.48	
$Eu(DBM)_3$, mechano-activated, 30 min	5.04	67.52	
$Eu(DBM)_3 \cdot$phen*	3.90	68.49	2.80
$Eu(DBM)_3 \cdot$phen, mechanoactivated, 30 min	4.77	73.02	1.68

** Theoretically expected*

spectrum of the 30 min-activated sample (Fig. 5.4). The appearance of a band at 519 cm^{-1} in the same spectrum that does not occur in the spectrum of the ligand (Fig. 5.1) has been taken as additional proof of the complexation [14]. Another proof is the band associated with Ln-O in diketonates [15] appearing at 420-430 cm^{-1}. The progress of the complexation process with activation time can be followed by comparison of the spectra, i.e. the development of the band at 1541 cm^{-1} and the decrease of the relative intensity and the "red" shift of the band at 758 cm^{-1}, which are specific for the complex and

Table 2. Crystallite sizes of the initial and mechanoactivated products.

Samples	Crystallites size (nm)			
	Not activated products	At activation time (min)		
		3	10	30
$EuCl_3 \cdot 6H_2O$	290	91	43	97
HDBM	60	43	45	63
$Eu(DBM)_3$	76	103		97
$Eu(DBM)_3 \cdot phen$	132			72

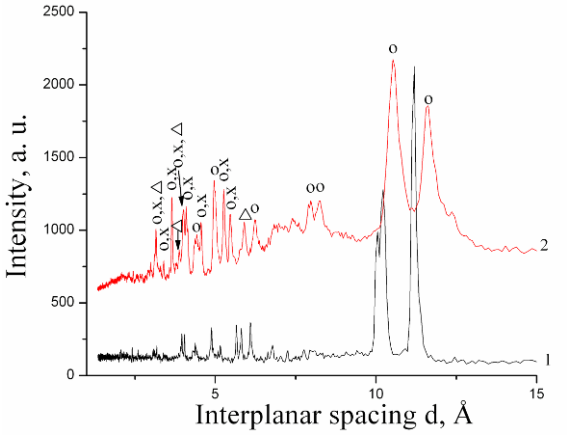

Figure 4. X-ray diffractograms of "wet" produced $Eu(DBM)_3 \cdot phen$ (1) and of $EuCl_3 \cdot H_2O$ – HDBM phen mixture (2) after 30 min mechanoactivation: o - $Eu(DBM)_3 \cdot phen$, x – HDBM, Δ – phen.

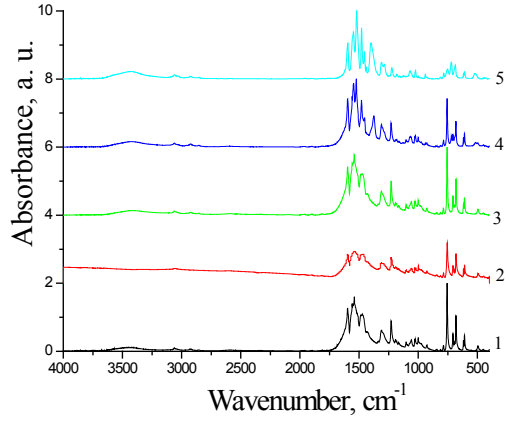

Figure 5. IR spectra of the initial HDBM (1), mechanoactivated HDBM (30 min, 2), and $EuCl_3 \cdot H_2O$ – HDBM mixture (3 min, 3; 30 min, 4) and "wet" prepared $Eu(DBM)_3$ (5).

for the free ligand, respectively. The IR spectrum does not give conclusive proof for the presence of water in the obtained complex: the band around 1630 cm^{-1} is missing and the weak band around 3434 cm^{-1} can be ascribed to traces of ethanol used in the purification of the activation products. The contribution of OH from the enol form of unreacted HDBM can not be excluded, even though no such form exists in pure activated HDBM (Fig 5.2).

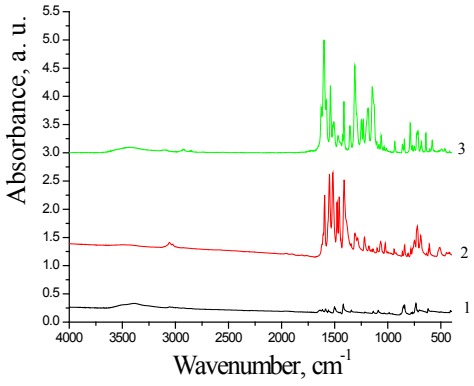

Figure 6. IR spectra of the initial phenanthroline (1), "wet" prepared $Eu(DBM)_3 \cdot phen$ (2) and 30 min-mechanoactivated $EuCl_3 \cdot H_2O$–HDBM-phen mixture (3).

IR spectra of the initial phenanthroline, "wet" prepared $Eu(DBM)_3 \cdot phen$ and 30 min-mechanoactivated $EuCl_3 \cdot H_2O$–HDBM-phen mixture are shown in Fig. 6; bands wave numbers are given in Table 3. The weak broad band around 3434 cm^{-1} and the one at 1627 cm^{-1} show the presence of water in the mechanosynthesis product. According to the thermogravimetric analysis, its content is ≤6% and is evolved among 60-220°C. The spectral data confirm the polyphase composition of the activated mixture, containing non reacted HDBM and phen along with the synthesized $Eu(DBM)_3 \cdot phen \cdot nH_2O$ and do not indicate the formation of $Eu(DBM)_3$ and $Eu(phen)_3$.

3.3. Optical properties

Excitation and emission spectra of some of the studied complexes in their solid state are shown in Figs. 7, 8. In Table 4, the maxima in the spectra are compared with those observed in the spectra of the same complexes prepared by conventional methods. The bands in the range of 200-400 nm in the excitation spectra are commonly attributed to absorption of the organic ligands (π-π* electron transition). The band at 300-400 nm is assigned to the DBM ligands [16,17]. The band at 348 cm^{-1} (attributed to HDBM-enol isomer, [14,15]) is red-shifted compared with the pure ligand (342 nm), which is similar to the observation in [14]. The excitation spectrum of $Eu(DBM)_3 \cdot phen$ (as solid, Fig. 7.2) is similar to the spectrum of the complex prepared by the common wet method proposed in Reference [11]. The addition of phenanthroline to $Eu(DBM)_3$ causes a small change of the position of the maximum in the spectra of the latter (Table 4), suggesting an insignificant perturbation in the DBM electronic system. This was already reported in [18] for the complex prepared by the common wet method.

Table 3. IR spectra of HDBM, o-phenatroline, $Eu(DBM)_3$·phen and mechanoactivated mixtures of $EuCl_3 \cdot 6H_2O$-HDBM and $EuCl_3 \cdot 6H_2O$-HDBM-phen.

Initial products		Mechanoactivated products			Initial products			Mechanoactivated products	
HDBM	1,10-Phenan-troline	$Eu(DBM)_3$·Phen	$EuCl_3$·$6H_2O$ -HDBM	$EuCl_3$·$6H_2O$ –HDBM - Phen	HDBM	o-Phenan-throline	$Eu(DBM)_3$·Phen	$EuCl_3$·$6H_2O$ –HDBM	$EuCl_3$·$6H_2O$ –HDBM - Phen
	3390	3459	3434	3435		1090	1098		1105
			3061			1076			1084
	1638	1618		1627			1066		1061
1600ws	1616	1609	1597	1600	1022w	1037			1034
1550sh	1587	1593	1558, 1524	1578	998w		1021	1025	1015
1541ws	1561	1550	1546	1539		988		1002	
		1516		1518	924w	958			
1470vs			1478	1469			940	940, 927	933
1455sh			1455			855			862
	1502			1507		840	840		843
	1445	1479					808		
	1419			1426		779			788
		1411		1413	758vs	767			769
		1390	1399					755	
	1344	1346		1336		735	747		
1307m		1311	1309	1308	705m		721	718	722
1285	1295	1283	1296	1293	680m	705		706	
		1255sh		1250			690	680	683
1228s	1215	1220	1230	1230			663		641
		1175			609w	623		617	
1101vw			1103				610	609	603
1056w			1067			589			580
		1157			494vw	508	510	514	
	1137	1139		1145				812, 498	490
				1128					

According to [17], the band at 210-300 nm with maximum around 250 nm is related to phenanthroline ligands. The presence of the typical absorption bands of the organic ligands in the excitation spectra confirms their coordination to the Eu^{3+}-ions.

The presence of a maximum around 450 nm (Fig. 7.1, 2) and rather weak peaks at 461 and 531 nm (Fig. 7.2) in the excitation spectra is a peculiarity observed for mechanoactivated products. Further investigations are needed to elucidate their origin. A similar excitation spectrum (recorded at 77 K) with a band at 612 nm is reported in [19] for $Eu(DBM)_3 \cdot H_2O$ with narrow bands corresponding to the Eu^{3+} ion centered $^7F_0 \rightarrow {}^5D_2$ (464 nm) and very weak $^7F_0 \rightarrow {}^5D_1$ (532 nm) and $^7F_0 \rightarrow {}^4G_6$ (578 nm) transitions. Similar bands were also observed in References [18,20]. A band at 443 nm is observed (as a shoulder) in the spectrum of $Eu(DBM)_3$ immobilized in hybrid silica-polyester matrix taken at ambient temperature [21].

The emission spectra of the 10^{-5} M dimethylformamid solutions of the "wet" produced $Eu(DBM)_3$ and of mechanoactivated products containing the same complex or $Eu(DBM)_3$·phen (excitation at 415 nm) are shown in Fig. 8. Along with the main maximum at 612 nm ($^5D_0 \rightarrow {}^7F_2$), the typical, much weaker bands at 573 ($^5D_0 \rightarrow {}^7F_0$), 592 ($^5D_0 \rightarrow {}^7F_1$), 650 ($^5D_0 \rightarrow {}^7F_3$) and 701 ($^5D_0 \rightarrow {}^7F_4$) nm are observed. The intensity of the photoluminescence decreases in the order $Eu(DBM)_3$·phen > $Eu(DBM)_3$ (both activated for 30 min) > $Eu(DBM)_3$, activated 3 min. It is seen that despite the

Table 4. Maxima (nm) in the excitation and emission spectra of some of the prepared complexes in solid state and luminescence lifetime (μs).

Sample	Excitation	Emission	Lifetime
$Eu(DBM)_3$ prepared from solution [4]	356, 374, 443, 418	566, 580, 585, 595, 612, 618, 625, 651, 700	137
$Eu(DBM)_3$ mechanosynthesized (3 min)	329, 339, 348, 388, 408, 450	566, 572, 596, 605, 610, 612, 673, 708	133
$Eu(DBM)_3$ mechanosynthesized (30 min)	408, 415, 450	570, 580, 589, 596, 610, 612, 670, 708	106
$Eu(DBM)_3$•phen prepared from solution [4]	265, 300, 325, 343, 397, 415	580, 585, 590, 597, 612, 618, 625, 650, 655, 695, 704	363
Eu $(DBM)_3$•phen mechanosynthesized (30 min)	329, 389, 408, 415, 450	595, 611, 615, 670, 708	442

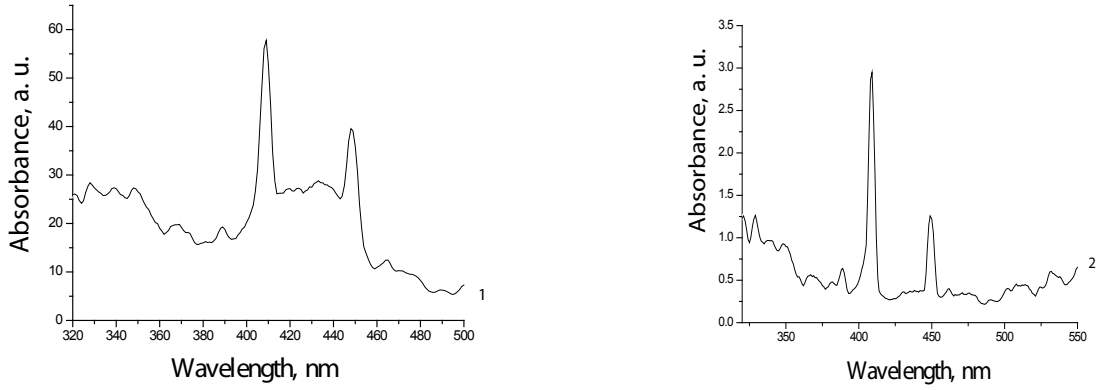

Figure 7. Excitation spectra of mechanoactivated products containing $Eu(DBM)_3$ (1, 3 min activation time) and $Eu(DBM)_3$•phen (2).

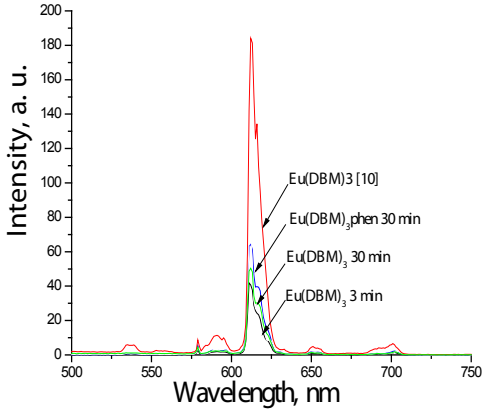

Figure 8. Emission spectra of the dimethylformamid solution of $Eu(DBM)_3$, produced by the "wet" method (1) and of mechanoactivated products containing $Eu(DBM)_3$, activation time: 3 min (1), 30 min (2) and $Eu(phen)_3$, activation time 30 min (3); excitation at 415 nm.

lower relative content of the diligand complex in the activated mixture compared to the content of $Eu(DBM)_3$ in the respective mechanoactivated product, the former shows a higher photoluminescence intensity. The order of the products containing monoligand complex is in accordance with their relative content in the activated mixture. As can be expected, the intensity of the mechanochemically produced samples remains lower than the one containing 100% of the complex.

The spectra of the solid substances containing $Eu(DBM)_3$ and $Eu(DBM)_3$.phen are shown in Fig. 9 and the maxima are listed in Table 4. No significant differences with the conventionally prepared complex are observed concerning the main bands. The emission spectra contain the typical (according to [17]) bands of Eu^{3+}. The band at 612 nm (Fig. 9.1) is slightly split, suggesting a relatively ordered Eu^{3+} environment. Indeed, the data for the observed luminescence lifetimes are perfectly fitted with single exponents (Fig. 10). This indicates that there is only one emission center in all of the studied specimens, so the Eu^{3+} environment must be ordered. An indication for the number of crystallographically non-equivalent sites in an europium(III) β-diketonate complex can be obtained from the number of lines observed for the $^5D_0 \rightarrow {}^7F_0$ transition. The presence of one line in the emission spectra of the obtained samples is an additional proof that the rare-earth ion is present in one single type of coordination polyhedron [1]. The bands of the $^5D_0 \rightarrow {}^7F_2$ transition are not broadened compared to the wet produced complex and the number of Stark components is preserved, which also confirms the relatively ordered environment of the Eu^{3+}.

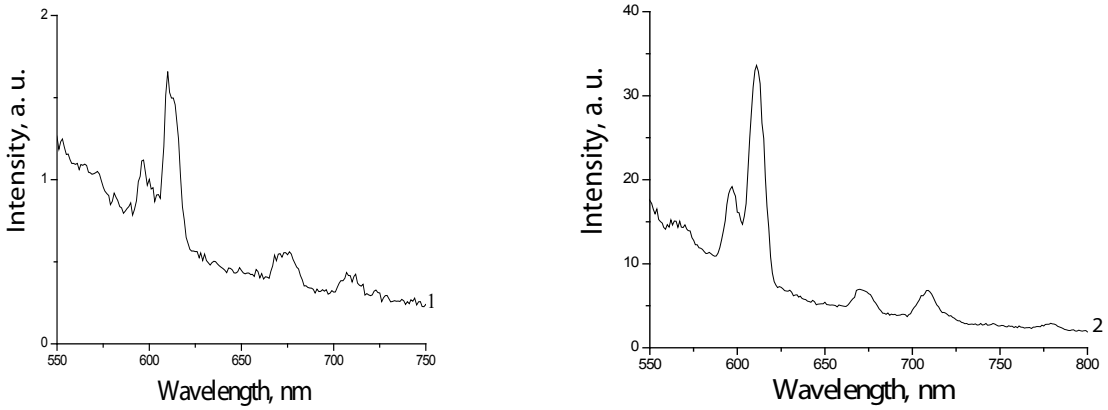

Figure 9. Emission spectra of mechanoactivated products containing $Eu(DBM)_3$ (1) and $Eu(DBM)_3$•phen (2); excitation at 415 nm.

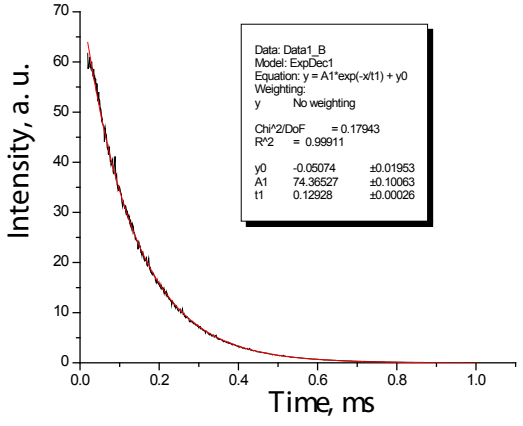

Figure 10. Luminescence lifetime of the mechanochemically produced solid $Eu(DBM)_3$•phen derived from the emission at 612 nm at ambient temperature; excitation at 415 nm.

The lifetimes of the excited states (in solid) of complexes produced by the conventional methods described in the Experimental section and by mechanosynthesis (Fig. 10) are rather close, and even longer for mechanically synthesized $Eu(DBM)_3$•phen (Table 4). The values obtained are in agreement with those reported in [22] and rather far away from the value of 1993 μs for $Eu(DBM)_3$ reported in [23].

The fluorescence of the products of mechano-activation in the solid state has the highest response to illumination when excited at 415 nm, while the complexes produced by the conventional methods are best excited at 410 nm. In solution, there is no difference. The phenomenon may be related with the effect of the mechanoactivation on the crystal structure of the synthesized products. The increased defects concentration as a result of the mechanical treatment

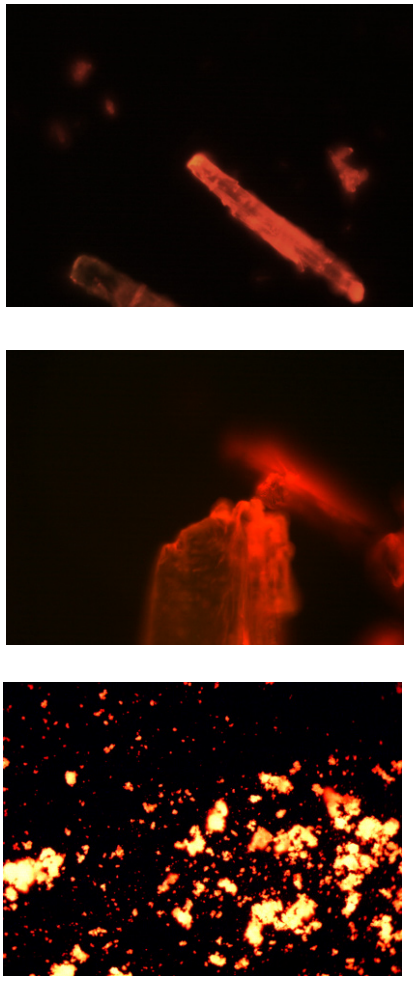

Figure 11. Fluorescence microscopy images (×640) of the products of mechanoactivation in the systems $EuCl_3$•$6H_2O$-HDBM, activation time 3 min (1), 30 min (2); $EuCl_3$•$6H_2O$-HDBM-phen, activation time 30 min (3).

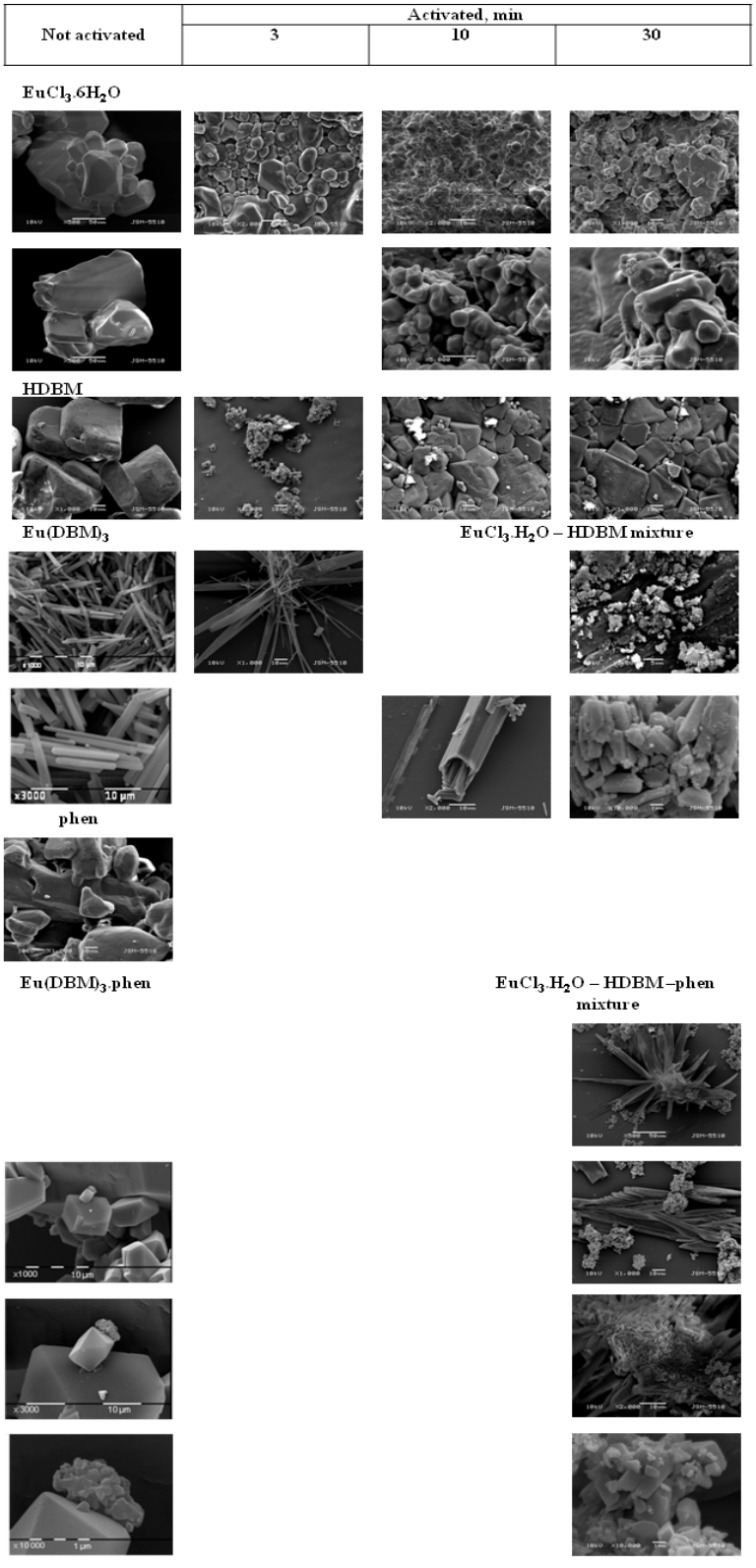

Figure 12. SEM images of the initial $EuCl_3 \cdot H_2O$, HDBM, phen, wet-produced $Eu(DBM)_3$ and $Eu(DBM)_3 \cdot$phen and mechanoactivated $EuCl_3 \cdot H_2O$, HDBM, mixtures $EuCl_3 \cdot H_2O$ – HDBM and $EuCl_3 \cdot H_2O$ – HDBM –phen.

may enhance the ligand excitation. The same effect may explain the increased "halo" in the emission spectra of the materials (Fig. 9) due to higher fluorescence of the unreacted ligand remaining in the studied samples.

3.4. Morphology

Fluorescence microscopy (Fig. 11) gives an overview of the morphology of the products of mechano-activation. Typical prismatic crystals of $Eu(DBM)_3$ are seen after 3 min activation. Agglomeration proceeds at longer activation time. The shapeless (at this magnification) crystals of $Eu(DBM)_3$•phen show rather high photoluminescence intensity.

SEM images of initial $EuCl_3$•$6H_2O$, HDBM and phen; $Eu(DBM)_3$ and $Eu(DBM)_3$•phen prepared by the method used in [4], as well as of the mixtures $EuCl_3$•H_2O - HDBM and $EuCl_3$•H_2O - HDBM – phen after different times of mechanoactivation are shown in Fig. 12.

Mechanoactivation for 3 min leads to strong fragmentation of the initial 40-60 μm-HDBM particles to 2-8 μm. Oval, 5-20 μm aggregates are formed after 10 min of activation, probably due to sintering because of the increased temperature and the lower melting point of the compound (76-78°C). The sintering continues at longer activation, leading to a rather broad (5-50 μm) size distribution of the particles formed.

The size of the $EuCl_3$•$6H_2O$ particles (some of them well shaped) decreases from 10-100 μm to 1-20 μm after 3 min activation and 1-5 μm after 10 min, and tend to agglomerate and increase in size to 5-20 μm at activation for 30 min.

Particles of rather different forms and size are observed in the activated $EuCl_3$•$6H_2O$-HDBM mixture: shapeless particles from 200 nm up to a few micrometers, prismatic crystals 1-10 μm in length and 1 μm in thickness, rather specific needle (0.2×few tens micrometers) or long-length-leaf - like particles (~ten - few tens micrometers) and rods ~10 μm in diameter.

At least two types of crystals are observed in the activated $EuCl_3$•$6H_2O$-HDBM-phen: leaf-like layered, similar but not the same as the above described for the phen-free system and prismatic (1 - 50 μm in length).

4. Conclusions

The results reported confirm the earlier finding of Kalinovskaya *et al.* and extend the knowledge on mechanoactivation as a tool for synthesis of lanthanide complexes with β-diketones. The applied procedure leads to production of a mixture of the respective complexes (whose content increases with activation time) with unreacted initial products. The produced materials have satisfactory fluorescence properties, manifested at illumination with longer-wave light in comparison with the complexes prepared by the conventional methods. Further efforts on improvement of the procedure, ensuring preparation of pure complexes by the applied route are necessary.

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