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A new continuous two-step molecular precursor route to rare-earth oxysulfides Ln_2O_2S

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ABSTRACT

A continuous two-step molecular precursor pathway is designed for the preparation of rare-earth oxysulfides Ln_2O_2S (Ln=Y, La, Pr, Nd, Sm–Lu). This new route involves a first oxidation step leading to the rare-earth oxysulfate $Ln_2O_2SO_4$ which is subsequently reduced to the rare-earth oxysulfide Ln_2O_2S by switching to a H_2–Ar atmosphere. The whole process occurs at a temperature significantly lower than usual solid state synthesis ($T \leq 650$ °C) and avoids the use of dangerous sulfur-based gases, providing a convenient route to the synthesis of the entire series of Ln_2O_2S. The molecular precursors consist in heteroleptic dithiocarbamate complexes [$Ln(Et_2dtc)_3$(phen)] and [$Ln(Et_2dtc)_3$(bipy)] (Et_2dtc=N,N-diethyldithiocarbamate; phen=1,10-phenanthroline; bipy=2,2′-bipyridine) and were synthesized by a new high yield and high purity synthesis route. The nature of the molecular precursor determines the minimum synthesis temperature and influences therefore the purity of the final Ln_2O_2S crystalline phase.

1. Introduction

Rare-earth oxide sulfides, commonly named oxysulfides in the literature (Ln_2O_2S, Ln standing here for rare-earth) are materials of undeniable interest from both the theoretical [1] and the technological points of view. Next to some minor applications like the catalysis of SO_2 reduction by CO [2], their main applications lie in the optical field: laser crystals [3], X-ray phosphors [4,5], long-lasting phosphorescent materials [6,7], red-emitting phosphors for TV screens [8,9], etc. Due to their closed-shell electron configuration, rare-earth elements such as Y, La, Gd and Lu can be selected to form Ln_2O_2S host materials that can then be doped by another lanthanide. For instance, the Eu^{3+}-doped yttrium oxysulfide $Eu_xY_{2-x}O_2S$, conventionally noted as Y_2O_2S:Eu^{3+}, has been largely used in TV screens due to its high luminescence performance [8,9].

The usual synthesis of Ln_2O_2S materials consists of solid state reactions under quite severe experimental conditions. Several methods have been reported, such as direct sulfidation of rare-earth oxides by sulfur-based gases such as H_2S [10,11], reduction of the rare earth sulfate by H_2 [12], or reduction of the rare earth sulfite by CO [13]. At the industrial level, the most important process is the so-called "sulfide-fusion method", which involves the use of a flux of elemental S, Na_2CO_3 and K_3PO_4 [14–16]. Unfortunately, most of those methods involve high temperatures (1100–1200 °C) and lead to contaminated materials that require to be washed ultimately with water and acids in order to remove the residual impurities [11,14–16]. Most of them also require the use of dangerous gases such as CO or H_2S under carefully controlled experimental conditions [10,11,13].

In the last 10 years, several alternative methods have been described in order to overcome these difficulties. A sol–gel pyrolysis route has been investigated [17,18] as well as the so-called "ethanol assisted combustion synthesis" [19,20]. The first one involves elemental sulfur in a urea–formaldehyde resin, while the second one relies on the use of thiourea or thioacetamide for the sulfidation. Dithiooxamide has also been used in a simple combustion synthesis [4]. However, as far as we know, only one example of single molecular precursor pathway has been reported so far for the synthesis of oxysulfides [21,22], while they are extensively described for the preparation of oxides or sulfides.

Molecular precursors methods offer several important advantages, especially for the preparation of phases with complex (i.e. multimetal) formulations. The final materials present most of the time excellent homogeneity due to initial mixing at the molecular level, and unwanted metal segregation is usually avoided thanks to chelating ligands [23,24]. In the case of oxides, the molecular precursor route often allows the synthesis to be carried out under milder conditions than other conventional methods [25,26].

Molecular precursors pathways have also been largely described for the preparation of metal sulfides, such as CdS [28,29], ZnS [27,28,30], Sb_2S_3 [31], Ni_3S_2 [27,32], and Bi_2S_3 [31,33–41], among

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others. The precursors used in these cases involve thiourea [29,36], thiosemicarbazide [29,36], thiolates [33,41], xanthates [32,37], thiophosphate [31] or the widely used dithiocarbamates [27,28,30,32,34,35,38–40]. In the case of rare earth elements, a major difficulty arises from their poor affinity for sulfur. For this reason, the availability of air-stable S-based rare earth complexes is quite limited. The only serious candidates are the heteroleptic compounds in which the N,N-dialkydithiocarbamate ligand is associated with bidentate nitrogen-donating ligands, in particular [$Ln(Et_2dtc)_3$(phen)] and [$Ln(Et_2dtc)_3$(bipy)] (where Et_2dtc refers to N,N-diethyldithiocarbamate, phen to 1,10-phenanthroline, and bipy to 2,2′-bipyridine), for which the syntheses have already been described in several papers [42-50]. These compounds have been successfully used for synthesis of rare earth sulfides [47].

The development of a suitable molecular precursor route for the synthesis of rare earth oxysulfides is even more complicated, due to the strong affinity of the rare earth elements for oxygen, contrasting with their poor affinity for sulfur. This is probably the reason why only one example of single molecular precursor pathway has been reported so far for the oxysulfides [21,22]. In this unique example, the thermolysis of a solution of [$Ln(Et_2dtc)_3$(phen)] complexes with oleic acid and oleylamine as surfactant was shown to be successful for Ln=Eu, Sm and Gd. The specific purpose of this work is to go one step further and investigate the possibility of synthesizing the oxysulfide directly from the molecular precursors in a solvent-free thermolysis synthesis, i.e. from solid state in an oven, without using other gaseous or solid sulfur sources than the ligand itself.

The synthesis of the selected molecular precursors ([$Ln(Et_2dtc)_3$(phen)] and [$Ln(Et_2dtc)_3$(bipy)]) has been reported in several papers [42–50]. The methods differ in lanthanide salts, namely chloride, perchlorate or nitrate, and solvents used, acetonitrile, ethanol, acetone and water among others. Almost all of them describe the synthesis for one or several lanthanides, with different conditions for each element. Interestingly, the present paper also describes a new uniform synthesis pathway for the [$Ln(Et_2dtc)_3$(phen)] and [$Ln(Et_2dtc)_3$(bipy)] complexes throughout the whole Ln series.

2. Experimental section

2.1. Materials and methods

All chemicals were purchased from commercial sources and used without further purification. Lanthanide trifluoromethanesulfonates (triflates) $Ln(CF_3SO_3)_3$ were purchased from Alfa Aesar for Dy, Tm, Yb, La, Sm and from Aldrich for Gd, Nd, Tb, Ho, Er, Eu, Pr, Lu. Diethylammonium N,N-diethyldithiocarbamate (Et_2NH_2)(Et_2dtc), came from Alfa Aesar, while 1,10-phenanthroline monohydrate (phen · H_2O) and 2,2′-bipyridine (bipy) were purchased from Acros. Elemental analyses were carried out by Medac Ltd, United Kingdom. Infrared spectra were recorded in the range of 400–4000 cm^{-1} on a Bruker Equinox 55 FT-IR spectrometer, using KBr pellets. Thermogravimetric analyses were performed in air at the heating rate of 100 °C/h on a TA Instruments SDT 2960 analyser. Powder X-ray diffraction (XRD) data were collected with a Siemens D5000 diffractometer using the Cu $K\alpha$ line (λ=0.15418 nm).

2.2. Complex synthesis

All the complexes were synthesized using the same procedure. As a typical synthesis, [$Gd(Et_2dtc)_3$(phen)] was obtained as follows. Diethylammonium diethyldithiocarbamate ((Et_2NH_2)(Et_2dtc), 12 mmol, 2.6690 g) was dissolved in 25 ml CH_3CN, then added dropwise to gadolinium trifluoromethanesulfonate ($Gd(CF_3SO_3)_3$, 4 mmol, 2.4178 g) previously partially dissolved in 55 ml CH_3CN. In the resulting clear mixture, 1-10 phenanthroline monohydrate (phen · H_2O, 4 mmol, 0.7929 g) was added dropwise. The solution was left under stirring during one hour. The precipitate was filtrated and washed by acetonitrile, then dried under vacuum at room temperature overnight.

The nature of each complex was checked by IR spectroscopy first. In the case of [$Ln(Et_2dtc)_3$(phen)], the relevant IR bands appear around 993–1007 cm^{-1} ($\nu_{C\text{-}S}$), 1482 cm^{-1} ($\nu_{C\text{-}N}$), 2975 cm^{-1} ($\nu_{C\text{-}H}$), and are attributed to the diethyldithiocarbamate ligand, while the bands around 730, 1517, 1572, 1589 and 1625 cm^{-1} correspond to phenanthroline [42,43]. For [$Ln(Et_2dtc)_3$(bipy)], the bands around 991–1008 cm^{-1} ($\nu_{C\text{-}S}$), 1483 cm^{-1} ($\nu_{C\text{-}N}$), 2974 cm^{-1} ($\nu_{C\text{-}H}$) are attributed to the diethyldithiocarbamate ligand and the bands around 771, 1564 and 1594 to the bipyridine ligand [42,43]. The nature and purity of all the complexes were also checked by elemental analyses, and are listed in Tables 1 and 2, together with the corresponding yields.

It seems interesting to point out that the concurrent attempts to synthesize these precursors from rare-earth nitrates in water (based on Ivanov's work [46]) gave us final products with very poor purity for Sm and Er and turned out to be totally unsuccessful for Tm, Lu and Y.

Table 1
Elemental analyses (%) and yields (%) for [$Ln(Et_2dtc)_3$(phen)] precursors.

Ln	Yield	C		H		N		S	
		Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
Y	75	45.43	45.63	5.36	5.36	9.81	9.95	26.95	27.06
La	86	42.45	42.33	5.01	4.98	9.16	9.19	25.18	24.29
Pr	89	42.34	42.37	5.00	5.09	9.14	9.19	25.12	25.18
Nd	93	42.16	41.91	4.98	4.76	9.10	8.80	25.01	24.66
Sm	90	41.83	41.60	4.94	4.87	9.03	9.04	24.81	24.78
Eu	92	41.74	41.53	4.93	5.02	9.01	9.24	24.76	24.87
Gd	94	41.46	41.26	4.90	5.11	8.95	9.29	24.60	24.54
Tb	92	41.37	41.19	4.89	4.75	8.93	8.76	24.54	24.51
Dy	77	41.18	40.57	4.86	4.87	8.89	8.76	24.43	24.14
Ho	90	41.05	40.81	4.85	4.67	8.87	8.89	24.35	24.58
Er	93	40.93	40.90	4.83	4.75	8.84	8.89	24.28	24.33
Tm	84	40.85	40.54	4.82	4.83	8.82	8.96	24.24	23.86
Yb	74	40.64	40.80	4.80	4.74	8.77	9.14	24.11	24.19
Lu	73	40.54	40.75	4.79	4.77	8.75	9.20	24.05	24.55

Table 2
Elemental analyses (%) and yields (%) for [$Ln(Et_2dtc)_3$(bipy)] precursors.

Ln	Yield	C		H		N		S	
		Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
Y	85	43.52	43.48	5.55	5.56	10.15	10.51	27.89	27.51
La	90	40.58	40.31	5.18	5.17	9.46	9.40	26.00	25.94
Pr	89	40.48	40.45	5.16	5.24	9.44	9.47	25.94	26.02
Nd	93	40.29	40.12	5.14	5.14	9.39	9.37	25.82	25.81
Sm	85	39.97	39.58	5.10	5.06	9.32	9.22	25.61	25.26
Eu	92	39.88	39.99	5.09	5.00	9.30	9.44	25.55	25.73
Gd	93	39.60	39.45	5.05	4.95	9.24	9.65	25.37	25.65
Tb	93	39.52	39.16	5.04	5.00	9.21	9.16	25.32	24.97
Dy	64	39.33	39.05	5.02	5.12	9.17	9.24	25.20	25.37
Ho	89	39.21	38.52	5.00	4.98	9.14	9.00	25.12	24.33
Er	89	39.09	39.01	4.99	4.97	9.11	9.12	25.05	24.93
Tm	61	39.00	38.54	4.97	4.91	9.09	9.21	24.99	24.48
Yb	66	38.79	38.62	4.95	4.94	9.04	9.09	24.85	23.56
Lu	23	38.70	37.94	4.94	5.02	9.02	8.76	24.80	23.07

2.3. Oxysulfide synthesis

The oxysulfide phases were obtained in a tubular oven according to the following procedure. [*Ln*(Et_2dtc)$_3$(phen)] or [*Ln*(Et_2dtc)$_3$(bipy)] powder was placed in a crucible and introduced in the oven. The first step consisted in heating up at 100 °C/h in an air-flux until 600 °C for [*Ln*(Et_2dtc)$_3$(phen)] or 500 °C for [*Ln*(Et_2dtc)$_3$(bipy)], then maintaining this temperature for 2 h. After intermediate flushing with nitrogen, the second step consisted in heating up at 100 °C/h until 650 °C in a H_2(5%)-Ar(95%) flux, then maintaining this temperature for 6 h. The oven came back to room temperature at 100 °C/h before recovering the sample.

3. Results and discussion

3.1. Precursor synthesis

Within the scope of this study, a major purpose was to design a rapid, easy and uniform synthesis for all the [*Ln*(Et_2dtc)$_3$(phen)] and [*Ln*(Et_2dtc)$_3$(bipy)] compounds. This could not be taken for granted despite the alleged homogeneity of rare earth properties. Indeed, the poor affinity of rare earth for sulfur decreases progressively while the hardness of the rare earth increases, i.e. from La to Lu. As far as we know, only one team reported the synthesis of all the rare earth complexes [42,43], starting from the corresponding perchlorates in acetonitrile. However, perchlorates need to be carefully handled being potentially explosive. In addition to that, most rare earth perchlorates are commercially available as aqueous solutions only implying a delicate drying step of the precursors before their use in anhydrous conditions.

For all those reasons, we decided to carry out the synthesis of [*Ln*(Et_2dtc)$_3$(phen)] and [*Ln*(Et_2dtc)$_3$(bipy)] from trifluoromethanesulfonates. These reagents combine the advantages of easy use (no particular precautions being required) and very poor coordination ability of the triflate ligand, with no competition against the rare-earth–sulfur coordination as a result. As detailed in the experimental section, the syntheses were successfully carried out in acetonitrile with generally excellent yield and purity, without need of recrystallization unlike other methods [44,45,47]. The experimental procedure was identical for all the Y, Pr–Nd, Sm-Lu rare earth elements, and for phen as well as bipy.

All the complexes obtained were characterized by IR spectroscopy and elemental analyses (see Section 2). Quite interestingly, when plotted versus the rare earth ionic radius the IR wavenumber corresponding to the stretching of the C-S bond (around 1000 cm^{-1}) exhibits a linear evolution for [*Ln*(Et_2dtc)$_3$(phen)] complexes (Fig. 1), showing that this bond is particularly sensitive to the nature of the coordinated rare earth. This evolution is less obvious for [*Ln*(Et_2dtc)$_3$(bipy)] due to the small splitting of this band.

3.2. Oxysulfide synthesis

The main purpose of this work is to synthesize pure rare earth oxysulfides by direct thermolysis of the selected molecular precursors, i.e. [*Ln*(Et_2dtc)$_3$(phen)] or [*Ln*(Et_2dtc)$_3$(bipy)] under appropriate atmosphere and temperature conditions. The first efforts were focused on the synthesis of lanthanide oxysulfides under air or nitrogen. However, while the preparation under pure nitrogen gave always the oxide sulfate, commonly named oxysulfate, $Ln_2O_2SO_4$, as the main phase, thermolysis under vacuum led to a mixture of oxysulfide and sulfide. In a recently published report, Boncher et al. [51] obtained similar results for the thermolysis of dithiocarbamate precursors under vacuum. All those experiments let us think that it would be extremely difficult to obtain pure

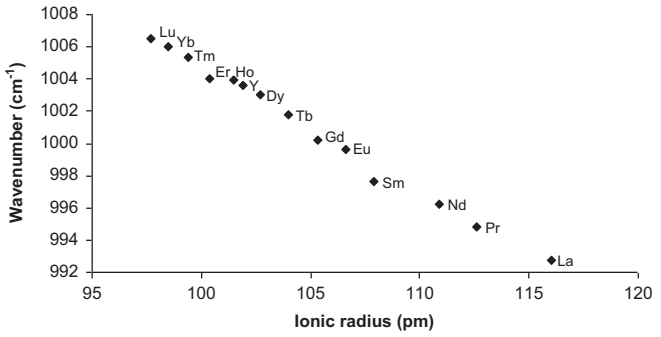

Fig. 1. Wavenumber corresponding to the stretching of the C–S bond plotted versus effective ionic radius (from R.D. Shannon, Acta Crystallogr. A32 (1976) 751) for [*Ln*(Et_2dtc)$_3$(phen)] complexes.

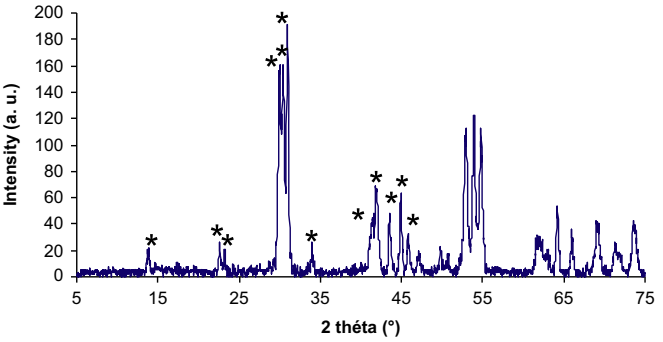

Fig. 2. Powder X-ray diffraction pattern of $Gd_2O_2SO_4$ obtained from [Gd(Et_2dtc)$_3$(phen)]. Identification via ICDD-JCPDS no. 29-0613.

Ln_2O_2S from dithiocarbamate precursors only by trying to control the amount of gaseous oxygen available, due to the high oxophilicity of the rare earth elements.

Nevertheless, considering that the oxysulfate could be obtained quite easily at a relatively low temperature after heating in air, and that this phase could be reduced under H_2 at ca. 800 °C [52–54], we designed a two-step continuous process in order to synthesize the rare-earth oxysulfide. Rather than trying to achieve direct lanthanide oxysulfide synthesis by a one-step molecular precursor combustion process, this work aimed for the readily obtained oxysulfate phase beforehand, this phase being easily reduced afterwards by using diluted H_2 atmosphere (H_2(5%)–Ar(95%)) at moderate temperature. The first attempts were made with [Gd(Et_2dtc)$_3$(phen)], Gd being selected for its potential ability to act as a host lattice for doped luminescent materials. The oxysulfate phase was observed after heating in air at 700 °C for 18 h (Fig. 2), then subsequently reduced into oxysulfide when switching to a H_2(5%)–Ar(95%) mixture during 6 h at the same temperature (Fig. 3).

The thermolysis process can be carried out continuously in the same tubular oven. Several attempts were carried out in order to determine the minimum temperatures required to observe the pure Gd_2O_2S phase. The minimum temperatures were found to be 500 °C and 650 °C for the first step in air and the second step under H_2(5%)–Ar(95%) mixture respectively. At lower temperatures, the thermolysis remains incomplete and leads to non-crystalline materials. Elemental analysis carried out on this sample showed that the residual contamination of the final materials by carbon and nitrogen was negligible (C < 0.1%, H = 0.66%, N = 0.39%).

This route was then tested for a few other lanthanides. The 500 °C first step temperature turned out to be too low for some lanthanides such as Nd, Sm, Tb, Dy, non-crystalline material being

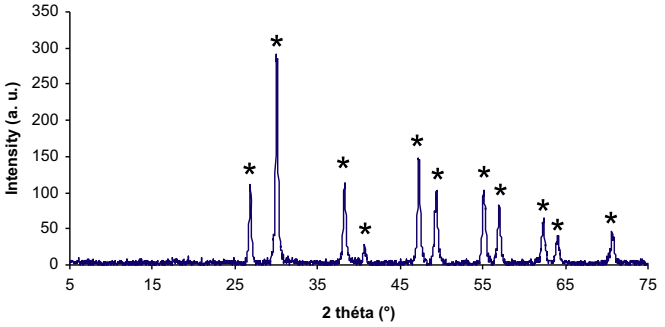

Fig. 3. Powder X-ray diffraction pattern of Gd_2O_2S obtained from [$Gd(Et_2dtc)_3$(phen)]. Identification via ICDD-JCPDS no. 26-1422.

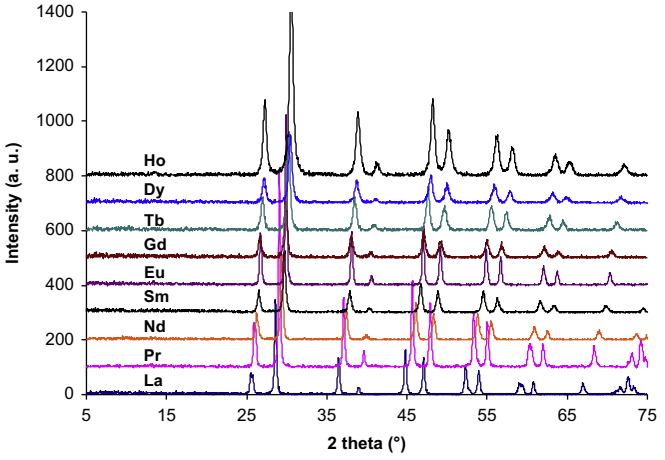

Fig. 4. Powder X-ray diffraction pattern of Ln_2O_2S obtained from [$Ln(Et_2dtc)_3$(phen)] (Ln=La, Pr, Nd, Sm–Ho). Identification via ICDD-JCPDS no. 27-0263 (La), 27-0479 (Pr), 27-0321 (Nd), 44-1257 (Sm), 26-1418 (Eu), 26-1422 (Gd), 26-1495 (Tb), 26-0592 (Dy), and 25-1143 (Ho).

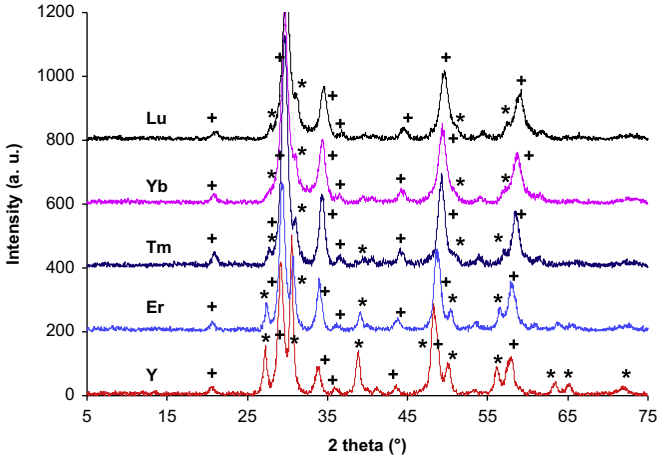

Fig. 5. Powder X-ray diffraction pattern of Ln_2O_2S phase (*) from [$Ln(Et_2dtc)_3$(phen)] (Ln=Y, Er–Lu). The (+) symbols refer to the Ln_2O_3 phase. Identification via ICDD-JCPDS no. 24-1424 and 41-1105 (Y), 25-1118 and 8-0050 (Er), 26-1389 and 41-1090 (Tm), 26-0614 and 41-1106 (Yb), 26-1445 and 12-0728 (Lu).

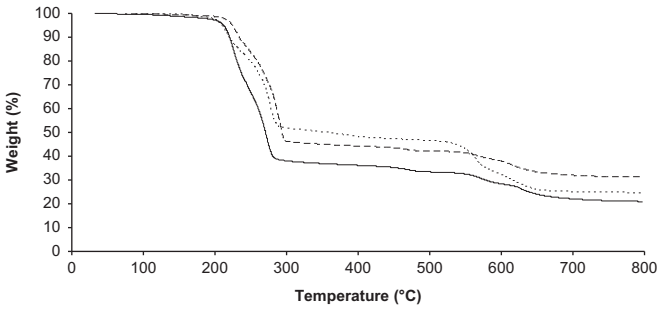

Fig. 6. Thermogravimetric analysis of [$Ln(Et_2dtc)_3$(phen)] in air. Ln=Y (solid line), Gd (dashed line), and La (dotted line).

observed in those cases. General conditions suitable for all the La, Pr, Nd and Sm-Ho elements were then determined. Pure crystalline phases were obtained for all these lanthanides from [$Ln(Et_2dtc)_3$(phen)] precursors in a continuous two-step process starting with heating in air at 600 °C for 2 h, followed by 6 h at 650 °C. The corresponding XRD patterns are shown in Fig. 4.

Er, Tm, Y, Yb and Lu complexes were also tested under the same conditions but they led to oxides as main phase and oxysulfide as minor phase, as shown in Fig. 5. This is probably due to the higher oxophilicity of the heavier lanthanides and yttrium. In addition to that, it came out that heating up the [$Y(Et_2dtc)_3$(phen)] precursor at 700 °C under air during 6 h led to a mixture of oxysulfate and oxide. This suggests that the oxide phase is not a degradation product from oxysulfide phase, but rather forms from the very beginning, during the first step in air. In the second step, the oxysulfate phase alone can obviously be reduced to oxysulfide under H_2. To obtain the pure oxysulfide phase, the idea of using a larger excess of sulfur in the rare earth surrounding was shown to be successful. Pure Y_2O_2S phase was indeed obtained in the presence of an excess of ammonium sulfate as external sulfur source.

The [$Ln(Et_2dtc)_3$(phen)] precursors were also studied by thermogravimetric (TG) analysis in order to study their decomposition pattern under air. Although the evolution of the TG curve depends on the nature of the element, general trends can be put forward. A first important and abrupt mass loss appears between 200 °C and 300 °C, possibly occurring in more than one step. A second gradual weight loss is observed between 500 °C and 700 °C, also occurring in several small steps. This behavior contrasts with the decomposition under N_2 as described in the literature [51], where only one single step was observed. Three representative curves have been plotted on Fig. 6 for La (similar tendency for Eu), Gd (similar evolution for Sm and Tb) and Y (similar trends for Dy–Lu). The nature of the intermediate plateau cannot be exactly determined: XRD measurements on the [$Gd(Et_2dtc)_3$(phen)] sample after heating at the temperature corresponding to the first plateau have shown an amorphous nature. The total weight loss is coherent with the formation of the $Ln_2O_2SO_4$ phase, possibly partially mixed with Ln_2O_3 phase for La, Dy, Er, Tm and Lu. The decomposition of Eu, Gd and Tb complexes seems to be partially incomplete according to the obtained weight losses (see Supplementary Information).

Several attempts to obtain $Ln_2O_2SO_4$ have also been carried out from [$Gd(Et_2dtc)_3$(bipy)] precursors. It soon appeared that the temperature required for the first step was lower than when starting from [$Gd(Et_2dtc)_3$(phen)]. Crystalline Gd_2O_2S was obtained by heating the bipy-based complex in air at only 150 °C for 2 h for the combustion step, the reduction step being carried out at the same temperature as with the other precursor. However, elemental analyses revealed in the latter case the presence of residual carbon (9.2%) and nitrogen (1.2%). To ensure completion of the combustion process, the other syntheses were carried out at 500 °C for the first step and 650 °C for the second one. The residual contamination of this Gd_2O_2S phase turned out to be negligible (C < 0.1%, H = 0.67%, N = 0.27%). Fig. 7 shows the XRD patterns for the whole Ln series.

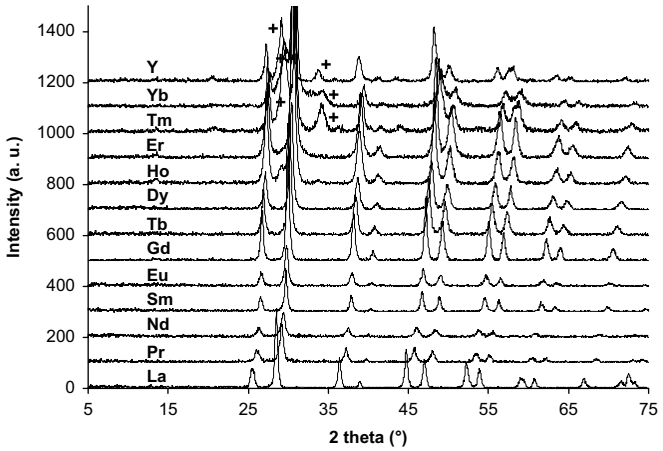

Fig. 7. Powder X-ray diffraction pattern of Ln_2O_2S from [Ln(Et_2dtc)$_3$(bipy)] (Ln=Y, La-Lu). The (+) symbols refer to the Ln_2O_3 phase.

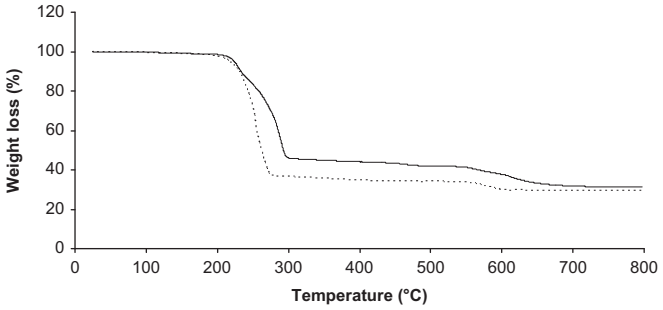

Fig. 8. Thermogravimetric analysis of [Gd(Et_2dtc)$_3$(phen)] (solid line) and [Gd(Et_2dtc)$_3$(bipy)] (dotted line) in air.

The formation of the pure Ln_2O_SS phase can be observed for all lanthanides but Tm and Yb. Interestingly for erbium, the diffractogram shows a pure Er_2O_2S phase, without traces of Er_2O_3, unlike from [Er(Et_2dtc)$_3$(phen)] (Fig. 5). This is probably due to the fact that the synthesis from [Er(Et_2dtc)$_3$(bipy)] was carried out at a lower temperature for the first step (500 °C instead of 600 °C for [Er(Et_2dtc)$_3$(phen)]). This lower temperature is assumed to prevent the formation of Er_2O_3, with the result that the pure $Er_2O_2SO_4$ phase can be reduced in Er_2O_2S afterwards.

TG analyses were also carried out for [Ln(Et_2dtc)$_3$(bipy)] complexes (see Supplementary Information). The decomposition scheme is characterized by a one-step weight loss around 250 °C, followed by a small weight loss around 600 °C for most of them. When comparing the thermogram of [Ln(Et_2dtc)$_3$(bipy)] and [Ln(Et_2dtc)$_3$(phen)] for each element, it appears that the first decrease of temperature occurs systematically at a lower temperature for the [Ln(Et_2dtc)$_3$(bipy)] complexes than that for [Ln(Et_2dtc)$_3$(phen)], and that the weight loss is systematically more important for [Ln(Et_2dtc)$_3$(bipy)] than for [Ln(Et_2dtc)$_3$(phen)], as shown for Gd in Fig. 8 for instance. This suggests that the degradation of [Ln(Et_2dtc)$_3$(bipy)] is easier than the one of [Ln(Et_2dtc)$_3$(phen)]: it begins at lower temperature and is more "complete" in the plateau between 300 °C and 500 °C (considering the bigger weight loss in this region). This could explain that crystalline Ln_2O_SS phases can be obtained at a lower temperature from [Ln(Et_2dtc)$_3$(bipy)] than from [Ln(Et_2dtc)$_3$(phen)], as mentioned previously, the thermal degradation of the phen ligand being probably not complete at 500 °C unlike in the case of bipy.

4. Conclusions

A convenient pathway to prepare the whole series of crystalline rare-earth oxysulfides Ln_2O_2S (Ln=Y, La, Pr, Nd and Sm–Lu) under the most moderate possible experimental conditions has been described. It is based on a continuous two-step process in which molecular precursors with mixed S–N coordination sphere, containing diethyldithiocarbamates and bidentate N-binding ligands such as bipyridine or phenanthroline, are first converted into the corresponding oxysulfates, which are further transformed into oxysulfides upon heating in a H_2/Ar mixture at 650 °C. Residual contamination of the final materials by carbon and nitrogen was found to be negligible. The applicability of this procedure to the whole series of rare-earth elements without any restriction opens the way to the preparation of a wide range of mixed phases that could be of high interest for tuning the luminescence properties of doped phases based on these lattices. In addition to that, the influence of the coordination sphere of the precursors on the minimum temperature required for the oxysulfide synthesis has been pointed out, demonstrating moreover the possibility of lowering this temperature by selecting adequate molecular precursors. In the case of Er more particularly, lowering the temperature proved to be an efficient way to improve the purity of the final material by preventing the formation of the unwanted Er_2O_3 phase. This work also describes a new high yield and high purity synthesis route to the molecular precursors themselves starting from the corresponding trifluoromethanesulfonate salts.

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Appendix A. Supplementary Information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.jssc.2012.03.017.

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