Low-temperature process of the cubic lanthanide sesquisulfides: remarkable stabilization of the γ-Ce_2S_3 phase

Stéphane Roméro,[a] Alain Mosset,[a] Jean-Christian Trombe*[a] and Pierre Macaudière[b]

[a] *C.E.M.E.S., 29, rue J. Marvig, B.P. 4347, F-31055, Toulouse Cedex, France*

[b] *Rhône-Poulenc Recherches, 52 rue de la Haie-Coq, F-93308 Aubervilliers, France*

Upon treating the corresponding oxalates with carbon disulfide ($p_{CS_2} = 130$ Torr) at a heating rate of 5 °C min^{-1}, it is shown that the cubic γ-phase of pure rare-earth sesquisulfides (γ-Ln_2S_3) can be obtained at 800 °C from samarium to holmium (also yttrium) and at 1000 °C from neodymium to dysprosium. By working on ternary sulfides $Ce_{2-x}Ln_xS_3$, it has been shown that the stabilization of the γ-phase occurs when the average ionic radius ranges between 1.015 and 1.104 Å at 800 °C. However, the nature of the observed sulfide phase also depends greatly on the experimental conditions, *i.e.* the nature of the precursor and the heating rate. At 800 °C and 5 °C min^{-1}, cerium oxalate leads to the β-phase while cerium nitrate leads to the α-phase. On the other hand, with cerium oxalate, the lower the heating rate the higher the amount of cubic γ-phase obtained.

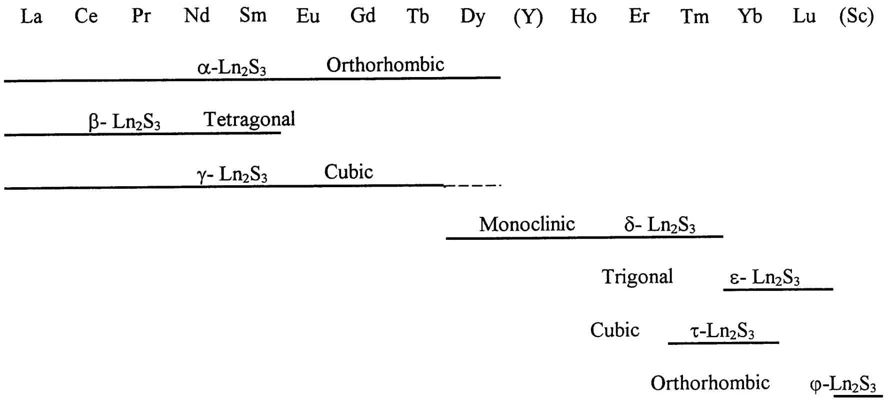
The sodium-doped γ-phase cerium sesquisulfide is used as a heavy-metal-free red pigment in plastics.[1–4] Scheme 1 gives a general overview of the lanthanide sesquisulfides. The light lanthanide sulfides have three polymorphic modifications:[5,6]

$$\alpha \xrightarrow{900\,°C} \beta \xrightarrow{1200\,°C} \gamma$$

However, these transformations remain somewhat controversial and mainly depend on the synthesis route. The α-form of Ln_2S_3 has a Gd_2S_3-type orthorhombic structure with *Pnma* space group.[7] The β-form is an oxysulfide, $Ln_{10}S_{15-x}O_x$ with $0 \leqslant x \leqslant 1$, that crystallizes in the tetragonal system.[8–11] The γ-phase is the high-temperature form and crystallizes in the cubic system (Th_3P_4 type, space group $I\bar{4}3d$).[12] The cations are randomly distributed over the available sites of the perfect lattice, because of the stoichiometry $Ln_{2.67}\square_{0.33}S_4$ where $\square_{0.33}$ represents the maximum number of metal vacancies. This phase exists over a wide range of compositions up to Ln_3S_4, without any significant variation in the cubic lattice constant. According to the literature data, this phase exists up to dysprosium (Scheme 1). However, its stabilization has been extended to the whole series of rare-earth elements (including yttrium) by using either high temperatures and pressures[13,14] or mechanical alloying.[15] With increasing atomic number from erbium to lutetium, the conditions to obtain such a metastable phase become harder and the γ-phase is often associated with stable δ and ε phases. The lattice parameters of γ-Ln_2S_3 (Ln = Dy–Lu), prepared by high-temperature and -pressure techniques, exhibit the normal lanthanide contraction while an expansion is observed for the samples synthesized by mechanical milling. This last phenomenon is not clearly understood.[15]

The usual synthesis route for the γ-phase consists of reacting the corresponding oxides with an H_2S flow at *ca.* 1200 °C for 2 hours, in the absence of moisture or oxygen;[5,6] in their presence, the β-phase is mainly obtained. Low-temperature syntheses of γ-Ln_2S_3 have been reported by treating, in a stream of H_2S at 1000 °C, either the light lanthanide oxycarbonates up to dysprosium (except for cerium)[16] or the lanthanum alkoxide[17] at sulfurization times of 5 or 8 h, respectively. It is worth noting that a low-temperature synthesis does not apply for γ-Ce_2S_3; indeed, cerium oxycarbonate does not exist.[18,19]

In a previous publication, we have shown that heavy lanthanide(III) elements used as dopants allow stabilization of the γ-phase of Ce_2S_3.[20,21] This stabilization is realized by heating a mixed precursor in H_2S for 1–2 h at low temperatures (600–800 °C). Poorly crystallized complexes such as carbonates, malonates or crystallized oxalates seem the most effective starting materials. Furthermore, stabilization requires a minimum Ln/Ce atomic ratio. The best element appears to be dysprosium followed by holmium, erbium and terbium. However, this stabilization is only transitory, heating above 800 °C yields again the β-form.



Scheme 1 Different allotropic forms of lanthanide sesquisulfides according to Guittard and Flahaut.[6] The β-form is considered wrongly as a sesquisulfide

The aim of the present paper is to characterize the sulfides obtained by treating the lanthanide complexes with carbon disulfide, at various temperatures and heating rates.[22] CS_2 is a powerful deoxygenating agent and its sulfurizing power is higher than that of H_2S.[23] The first section presents a general aspect of the binary and the ternary sulfides obtained with a normal heating rate ($v = 5\ °C\ min^{-1}$). The ternary system consists of a cerium component along with a second lanthanide. In the second section, the unusual effect of the heating rate on the nature of the observed phases is emphasized through some examples of binary and ternary systems. Single or mixed oxalates were used for all the studies.

Experimental

The single or mixed lanthanide oxalate(s) were prepared by reacting a solution of the corresponding nitrate(s) with a solution of oxalic acid present in a slight excess, at ambient temperature. The precipitates were filtered, washed with distilled water and dried at room temperature. About 500 mg of the starting product, contained in a mullite boat, were placed into a silica tube within the furnace. The tube was purged with nitrogen for *ca.* 12 h. Then nitrogen was bubbled through liquid carbon disulfide (analytical grade with $H_2O \leqslant 0.03\%$) maintained at 0 °C ($p_{CS_2} \approx 130$ Torr). The flow rate of nitrogen, carefully controlled by a flow meter ($25\ ml\ min^{-1}$), was kept constant during the whole experiment until cooling at ambient temperature. The heating rate of the furnace was varied in the range $0.3–50\ °C\ min^{-1}$. The maximum temperature was then retained for usually 1 h. Then the furnace was shut off and allowed to cool.

In some cases, the starting oxalates (Dy/Ce) were fired at 300 °C in air for 24 h, prior to sulfurization.

Powder X-ray diffraction patterns were obtained using a Seifert XRD3000 diffractometer (Cu-Kα radiation) and compared to JCPDS files. When different phases were observed, their relative amounts were determined by comparing the main reflections. The IR spectra were obtained on KBr pellets using a Perkin-Elmer FT-IR 1725 X instrument. For the ternary samples, the observed phases are denoted γ- or β-Ce_2S_3 although they may contain another lanthanide element.

At either synthesis temperature (800 or 1000 °C), all the sulfides obtained are black. Some were analysed for C, S and Ln and O content estimated by difference. The percentage of carbon ranges from 2 to 4 mass%. This impurity may originate either from the precursor or from the sulfurizing reagent. At these temperatures, carbon disulfide is known to release carbon.[24] More interestingly, the oxygen content is relatively high: at 800 °C, it ranges from 2 to 4 mass% while for Ce it reaches 9 mass%. At 1000 °C %O decreases (0.8–3 mass%; Ce, 4.7 mass%). These values are clearly higher than the content of oxygen in the pure β-phase (*ca.* 0.8 mass%). Similarly, the S/Ln ratio (1.5–1.6) is always slightly higher than the stoichiometric values [1.33 (Ce_3S_4)–1.5 (Ce_2S_3)]. The S/Ln ratio decreases with increased treatment temperature but still remains >1.5. This observation may be explained by traces of polysulfides S_n^{2-} ($n \geqslant 2$) adsorbed on the surface of the particles; at the treatment temperatures used, some polysulfides are known to exist.[21] The presence of oxygen is explained by considering the IR spectra of these sulfides which show the presence of sulfate groups and the proportion of these decreases with increased temperature. Sulfates are probably adsorbed on the surface of the particles and no traces of crystallized sulfate phases were identified by XRD. The high content of oxygen in cerium sulfide appears anomalous but cerium is well known to behave differently from the other lanthanides.[5,6]

Results and Discussion

Although the oxalates were prepared at ambient temperature they are well crystallized. The mixed-lanthanide oxalates are the 'decahydrates' $[Ln(H_2O)_3]_2(C_2O_4)_3{\cdot}4H_2O$, the single oxalates of Y, Tm and Lu are the 'hexahydrates', $[Ln(H_2O)_2]_2(C_2O_4)_3{\cdot}2H_2O$, following the terminology usually used for these complexes.[25,26] The nature of the precursors, fired in air at 300 °C for 24 h, depends on the atomic ratio Ln/Ce (*cf.* Table 4). In the case Ln = Dy, the X-ray diffraction powder pattern of the sample containing dysprosium alone reveals the presence of an amorphous phase while poorly crystallized ceria (CeO_2) is observed for the samples with Dy/Ce ⩽ 1.50. IR data show the presence of oxalate and carbonate ligands for the pure dysprosium sample, with more oxalate than carbonate groups present. When the atomic ratio Dy/Ce is in the range 1.50–0.25, only carbonate groups remain and are at a decreased level. For the pure cerium sample no carbonate groups are evident. Such observations are in agreement with the thermal behaviour of the oxalate complexes. Owing to the transformation $Ce^{III} \rightarrow Ce^{IV}$, pure cerium oxalate is fully decomposed at 300 °C while higher temperatures are needed to decompose pure dysprosium oxalate (650 °C).[18,27]

Sulfurization process at a heating rate of $5\ °C\ min^{-1}$

Binary sulfides. The sulfurization process was carried out on the lanthanide oxalates at 800 and 1000 °C for 1 h with CS_2, ($v = 5\ °C\ min^{-1}$) and results are reported in Table 1.

At 800 °C, the pure β-form is obtained for lanthanum and cerium, [Fig. 1(*a*)]. A mixture of β and γ phases is present for the two following elements, praseodymium and neodymium, but with the γ-phase predominating. From samarium to holmium, the γ-phase only is observed [Fig. 1(*b*)]. For erbium, the γ-phase is associated with a monoclinic phase (F-Er_2S_3 type[28–30]), different from the δ-phase [Fig. 1(*c*)]. For thulium, a mixture of phases is observed, Tm_2O_2S and an unknown phase.

The lattice parameters of the cubic γ-phase are compared to those found in the literature data (Table 2). A fair agreement is noted for the lighter lanthanides (Pr–Gd) while for the heavier rare earths (Tb–Er) our values are significantly higher than those observed by Eatough *et al.*[13] but smaller than those obtained by Han *et al.*[15] However, our values follow the so-called lanthanide contraction. Note that for europium, both EuS and (mixed-valence) Eu_3S_4 are observed due to facile reduction. The cell parameter of this last compound is similar to that obtained in other work [8.536(1) *vs.* 8.537 Å[31]].

At 1000 °C, no fundamental change is observed for the lighter lanthanides, La, Ce and Pr. The pure cubic phase is observed from neodymium to dysprosium and is associated to the δ-phase for holmium. The δ-phase is pure for yttrium but for the heavier lanthanides, Er and Tm, a mixture of phases is present (Table 1).

These results clearly demonstrate that the existence of the β, γ and δ sulfides is mainly a function of the temperature. To our knowledge, the formation of the pure γ-phase at 800 °C for the lanthanide elements from Sm to Ho has not been reported. The results can be explained by the use of complex precursors, which become amorphous upon decomposition, reacting with the very powerful sulfurizing agent, CS_2.

The question arises as to whether the existence of the cubic γ-phase is limited only by the ionic radius of the lanthanide elements. Using this assumption, and at 800 °C, the ionic radius would appear to have to be between that of samarium and holmium.[32]

$$r_{Ho^{3+}} = 1.015 < r_{Ln^{3+}}/\text{Å} < 1.079 = r_{Sm^{3+}}$$

At 1000 °C, lower and upper limits of the ionic radius are shifted towards higher values: $r_{Dy^{3+}} = 1.027 < r_{Ln^{3+}}/\text{Å} < 1.109 = r_{Nd^{3+}}$. The results at 1000 °C are thus in better agreement with the literature data.[16]

Table 1 Lanthanide sulfides obtained by treating the corresponding oxalates. Treatment conditions: CS_2, 1 h, $v = 5\,°C\,min^{-1}$

	observed phases				
Ln	$T = 800\,°C$	a_γ/Å	$T = 1000\,°C$	a_γ/Å	$r_{Ln^{3+}}$/Å[32]
La	β-La_2S_3		β-La_2S_3		1.160
Ce	β-Ce_2S_3		β-Ce_2S_3		1.143
Pr	γ-$Pr_2S_3 > \beta$-Pr_2S_3 (30%)	8.575(4)	γ-$Pr_2S_3 > \beta$-Pr_2S_3 (30%)	8.582(1)	1.126
Nd	γ-$Nd_2S_3 > \beta$-Nd_2S_3 (20%)	8.529(3)	γ-Nd_2S_3	8.532(1)	1.109
Sm	γ-Sm_2S_3	8.457(3)	γ-Sm_2S_3	8.449(2)	1.079
Eu	$EuS + Eu_3S_4$	8.536(1)	EuS		1.066
Gd	γ-Gd_2S_3	8.386(3)	γ-Gd_2S_3	8.389(3)	1.053
Tb	γ-Tb_2S_3	8.347(5)	γ-Tb_2S_3	8.345(3)	1.040
Dy	γ-Dy_2S_3	8.313(6)	γ-Dy_2S_3	8.306(3)	1.027
Y	γ-Y_2S_3	8.321(3)	δ-Y_2S_3		1.019
Ho	γ-Ho_2S_3	8.290(4)	γ-$Ho_2S_3 + \delta$-Ho_2S_3	8.277(3)	1.015
Er	γ-Er_2S_3 + F-Er_2S_3[a]	8.271(4)	δ-Er_2S_3 + F-Er_2S_3[a]		1.004
Tm	Tm_2O_2S + unknown phase		Tm_2O_2S + F-Tm_2S_3[a] + δ-Tm_2S_3		0.994

[a] This phase is monoclinic.[29–31]

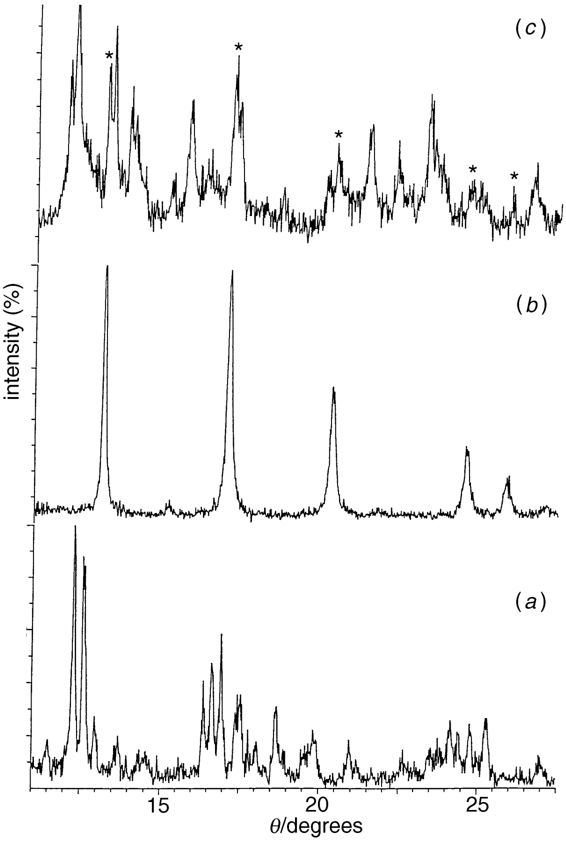


Fig. 1 X-Ray powder diffraction patterns of lanthanide sulfides obtained at 800 °C by treating the corresponding oxalates in the conditions defined in Table 1: (*a*) cerium β-phase; (*b*) holmium γ-phase; (*c*) erbium γ and F-Er_2S_3 phases. When different phases are observed, the reflections of the γ-phase are indicated by * in all figures.

Table 2 Lattice parameters of some lanthanide cubic sesquisulfides

	a/Å			
	present study	Picon *et al.*[31]	Eatough *et al.*[11]	Han *et al.*[15]
γ-La_2S_3	—	8.731		
γ-Ce_2S_3	—	8.630		
γ-Pr_2S_3	8.575(4)	8.573		
γ-Nd_2S_3	8.529(3)	8.527		
γ-Sm_2S_3	8.457(3)	8.448		
Eu_3S_4	8.536(1)	8.537		
γ-Gd_2S_3	8.386(3)	8.387		
γ-Tb_2S_3	8.347(5)	8.334		
γ-Dy_2S_3	8.313(6)	8.292		
γ-Y_2S_3	8.321(3)		8.306	8.340
γ-Ho_2S_3	8.290(4)		8.245	8.308
γ-Er_2S_3	8.271(4)		8.244	8.358
γ-Tm_2S_3	—		8.225	8.349
γ-Yb_2S_3	—		8.224	8.358
γ-Lu_2S_3	—		8.198	8.435

Ternary sulfides. As previously reported, dysprosium was the most efficient additive in stabilizing the γ-Ce_2S_3 phase under H_2S treatment.[20] We thus studied this element first.

Cerium–dysprosium sulfide. We used as starting material either the mixed-lanthanide oxalates or the same oxalates previously fired at 300 °C in air for 24 h and studied the influence of the atomic ratio Dy/Ce on the nature of the observed phases (α, β or γ). The corresponding results are gathered in Tables 3 and 4, respectively.

For oxalate precursors, the β-phase occurs in conjunction with the γ-phase at low Dy/Ce ratio (*e.g.* 0.25) and only traces of the β-phase are observed for Dy/Ce = 0.5 (Table 3). At higher Dy/Ce ratios, the γ-phase is exclusively formed as found for dysprosium alone. The introduction of dysprosium ($r_{Dy^{3+}} = 1.027$ Å *vs.* $r_{Ce^{3+}} = 1.143$ Å[32]) reduces the lattice parameters and Vegard's law is observed (Fig. 2).

If, as we postulated previously, the presence of pure γ-phase is related to the ionic radius of the lanthanide, the mean radius $r_m = [(2-x)r_{Ce} + xr_{Dy})/2$ should be used for mixed lanthanide sulfides. Since the γ-phase appears to be pure for Dy/Ce = 0.50, thus for $r_m = 1.104$ Å, this led us to increase the upper limit of the range of the ionic radius defined previously, at 800 °C: $1.015 < r_{Ln^{3+}}/\text{Å} < 1.104$.

For fired precursors, the only phase observed is the Gd_2S_3 type α-form,[7,33] with the exception of dysprosium alone (Dy/Ce = ∞, Table 4, Fig. 3). For this latter compound this phase also appears but in smaller amounts than for the γ phase. The cell volume of the α-phase as a function of the atomic ratio Dy/Ce is almost linear and a continuous range of homogeneity is observed from Ce_2S_3 to Dy_2S_3 (Fig. 4). This system was previously studied by Carré, at temperatures of 1000–1100 °C, and a limited solid solution was observed,[29,34] however the precursors and treatment conditions were different.

By comparing the results of Tables 3 and 4, the change of precursors (fired or not) largely modifies the nature of the obtained sulfides. Two main features are worth noting, concerning the two extreme points, pure cerium and dysprosium respectively.

For dysprosium, starting with an appreciable amount of carbon (oxalate) favours the γ-phase while the α-form begins to appear by decreasing slightly the proportion of carbon

Table 3 Sulfurization at 800 °C of $Ce_{2-x}Dy_x(C_2O_4)_3{\cdot}10H_2O$. Treatment conditions as in Table 1

Dy/Ce	0	0.25	0.50	1.00	1.50	3.00	∞
observed phases	β-Ce_2S_3	γ-Ce_2S_3, β-Ce_2S_3[a]	γ-Ce_2S_3, β-Ce_2S_3[b]	γ-Ce_2S_3	γ-Ce_2S_3	γ-Ce_2S_3	γ-Dy_2S_3
a_γ/Å		8.579(4)	8.549(7)	8.504(7)	8.457(7)	8.412(5)	8.313(6)
r_m/Å	1.143	1.120	1.104	1.085	1.073	1.056	1.027

[a]Minor component. [b]Trace.

Table 4 Sulfurization at 800 °C of $Ce_{2-x}Dy_x(C_2O_4)_3{\cdot}10H_2O$ previously fired at 300 °C for 24 h in air. Treatment conditions as in Table 1

Dy/Ce	0	0.25	0.50	1.00	1.50	3.00	∞
precursor	CeO_2	CeO_2	CeO_2	CeO_2	CeO_2[a]	CeO_2[a]	amorphous
mass % C of precursor	<0.1	<0.1	1.00	2.33	2.73	6.43	9.45
observed phases	α-Ce_2S_3	α-Ce_2S_3	α-Ce_2S_3	α-Ce_2S_3	α-Ce_2S_3	α-Ce_2S_3	γ-Dy_2S_3, α-Dy_2S_3[b]
a_γ/Å							8.316(6)
V_α/Å^3	483.7(3)	472.0(4)	466.1(4)	456.2(6)	451.4(7)	442.7(3)	428.3(4)
r_m/Å	1.143	1.120	1.104	1.085	1.073	1.056	1.027

[a]Very badly crystallized. [b]Minor component.

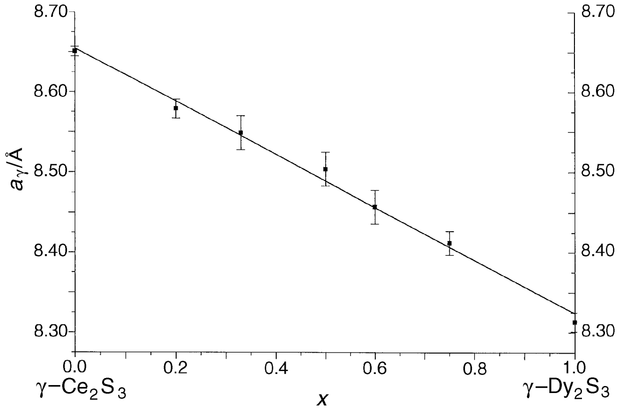


Fig. 2 Evolution of the lattice constants of the cubic phase *vs.* the atomic ratio Dy/Ce. The point $x=0$ (Dy/Ce = 0) is given in Table 6. Correlation coefficient = −0.9969.

(fired precursor). This is in line with the assertion of Cutler *et al.* who suggested that carbon stabilizes the γ-phase[35] although this explanation is controversial.[36]

For cerium, the amount of carbon has almost the opposite effect: cerium oxalate leads to the β-form while the fired precursor (ceria practically free of carbon, Table 4) yields the α-form. This last form is also obtained by the sulfurization treatment of the cerium nitrate, under the same conditions at either 800 or 1000 °C. At the latter temperature, such a phase is uncommon. The presence of the β-phase appears as a consequence of the decomposition of cerium oxalate and once this phase is formed it is very difficult to transform. Investigations on the effect of carbon on the formation of cerium sesquisulfide are currently in progress.[37]

One important feature is the stabilization of γ-Ce_2S_3 up to Dy/Ce = 0.50 at 800 °C. We thus conducted studies for the remainder of the lanthanide elements.

Ce–Ln sulfides with Ln = La–Lu (including Y). Sulfurization was performed for the mixed oxalates (Ln/Ce = 0.50) under the conditions used for Dy and results are listed in Table 5. When the doping element is lanthanum, only the β-phase was obtained. Traces of the γ-phase were observed for praseodymium and neodymium while for samarium the γ-phase predominated over the β-phase. Thus, the smaller the lanthanide element, the larger the amount of the γ-phase over the β-phase. The β-phase is still present in traces for dysprosium but is absent for erbium and thulium, although pure γ-Er_2S_3 and γ-Tm_2S_3 do not exist under such conditions.

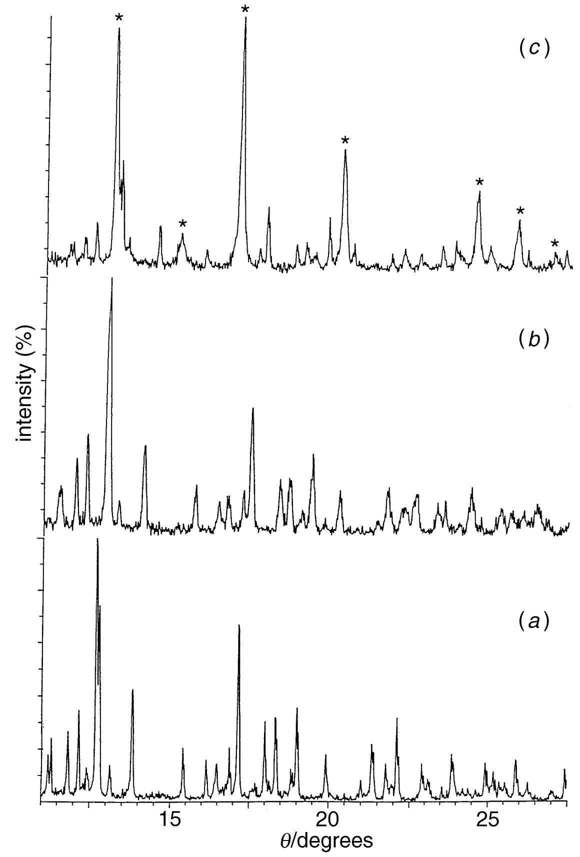


Fig. 3 X-Ray powder diffraction patterns of cerium–dysprosium sulfides obtained by treating the cured precursors in the conditions defined in Table 4: (*a*) Ce α-phase; (*b*) Dy/Ce = 1 α-phase; (*c*) Dy γ and α phases

The mean ionic radii for the γ-$Ce_{1.33}Ln_{0.67}S_3$ with Ln = Er and Tm are 1.097 and 1.093 Å, respectively. These last values are within the range of r_m previously estimated. This is in good agreement with the existence of a relation between the stability of the γ-phase and the mean ionic radius of the lanthanide under our conditions (CS_2, $v = 5$ °C min^{-1}, 800 °C, 1 h).

As expected, the introduction of lanthanide elements with an ionic radius smaller than Ce^{III} has the effect of decreasing the cell parameters of the γ-phase. Two exceptions are europium and thulium; while for europium this is caused by facile reduction to the divalent state {the cell parameter found

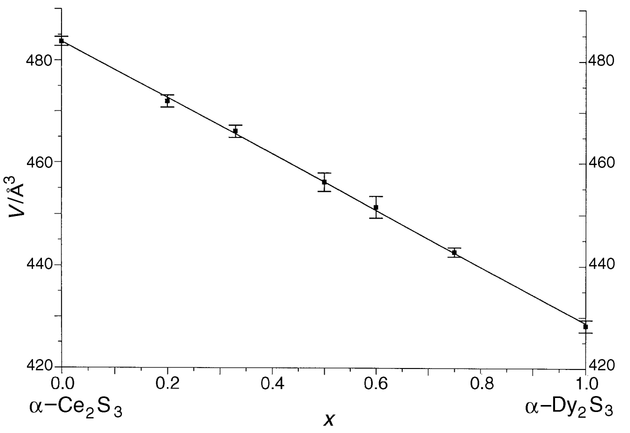


Fig. 4 Evolution of the volume of the α-phase *vs.* the atomic ratio Dy/Ce. Correlation coefficient = −0.9996.

Table 5 Sulfurization at 800 °C of $Ce_{1.33}Ln_{0.67}(C_2O_4)_3{\cdot}10H_2O$. Treatment conditions as in Table 1

Ln	observed phases[a]	a_γ/Å	V_β/Å^3	r_m/Å
La	β-Ce_2S_3		4906	1.149
Pr	β-$Ce_2S_3 \ggg \gamma$-Ce_2S_3 (trace)		4842	1.137
Nd	β-$Ce_2S_3 \ggg \gamma$-Ce_2S_3 (trace)		4790	1.132
Sm	γ-$Ce_2S_3 > \beta$-Ce_2S_3 (*ca.*40%)	8.580(4)	4772	1.122
Eu	γ-Ce_2S_3	8.682(2)		1.117
Gd	γ-$Ce_2S_3 \gg \beta$-Ce_2S_3 (*ca.*20%)	8.566(9)		1.113
Tb	γ-$Ce_2S_3 \gg \beta$-Ce_2S_3 (*ca.*20%)	8.564(9)		1.109
Dy	γ-$Ce_2S_3 \ggg \beta$-Ce_2S_3 (trace)	8.549(7)		1.104
Er	γ-Ce_2S_3	8.548(8)		1.097
Tm	γ-Ce_2S_3	8.559(4)		1.093

[a] The amount of the observed phases is estimated by comparing their major XRD reflections.

in this study [8.682(2) Å] is near to the value assigned to $EuCe_2S_4$ (8.685 Å)[38]} no valid explanation is apparent for thulium.

Influence of the heating rate

Among the studies of lanthanide sulfides, the effect of the heating rate on the nature of the observed phases has scarcely been considered although a recent study underlines its influence. Sulfurization of $Nd_2(SO_4)_3$, using CS_2 at 1100 °C, led to γ-Nd_2S_3 together with the α-phase when the heating rate was 10 °C min^{-1}. In contrast, at lower heating rates of 1 and 5 °C min^{-1}, the pure α-phase was obtained.[23]

We studied the effect of this factor on pure cerium and dysprosium oxalates and on the mixed (cerium–dysprosium) oxalates.

Binary sulfides. For cerium oxalate, sulfurization at 800 °C and a heating rate of 5 or 30 °C min^{-1}, leads to the pure β-form [Table 6, Fig. 5(*a*)] while at lower rates of 1 and 0.3 °C min^{-1}, the γ-phase is obtained at the expense of the β-form [Fig. 5(*b*) and (*c*)]. The question arises as to whether the formation of the cubic phase is a result of a decrease of the heating rate or of an increase of the treatment time. An experiment at $v = 1$ or 0.3 °C min^{-1} takes 14 or 44 h, respectively, *vs.* 3 h 40 min at $v = 5$ °C min^{-1}. We thus decided to maintain a plateau of 800 °C for 36 h while retaining a heating rate of 5 °C min^{-1}. Under these conditions β-Ce_2S_3 was the only observed phase. This observation clearly shows that the formation of the cubic phase depends only on the heating rate: the lower this is (<5 °C min^{-1}) the higher the proportion of the γ-phase.

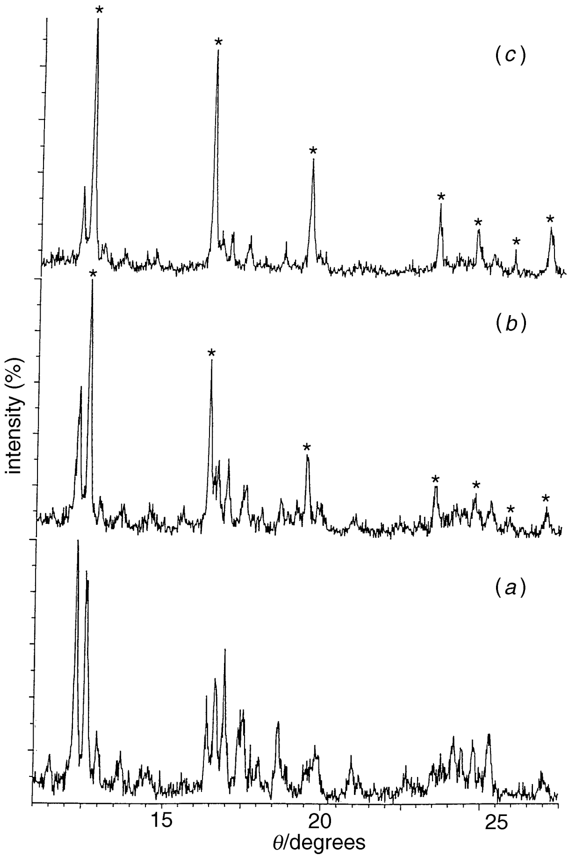


Fig. 5 X-Ray diffraction powder patterns of cerium sulfides obtained by treating the corresponding oxalate as a function of the heating rate (the conditions of treatment are defined in Table 6): (*a*) $v = 5$ °C min^{-1}, pure β-phase; (*b*) $v = 1$ °C min^{-1}, β and γ phases; (*c*) $v = 0.3$ °C min^{-1}, γ and β phases

It is worth noting the modification of the cell volume of the β-form. This phase is an oxysulfide, $Ce_{10}S_{15-x}O_x$ with $0 \leqslant x \leqslant 1$, the structure of which has been solved for $x = 1$[11] [a = 15.2124(4) Å, c = 20.1843(9) Å, V = 4671 Å^3]. At a heating rate of 30 °C min^{-1}, the volume is 4669(5) Å^3, close to the formulation with $x = 1$ while for 5 °C min^{-1} or less it ranges from 4865 to 4902 Å^3, depending on the time of treatment. While some sulfur atoms can replace oxygen, the limit $x = 0$ is not known, and may well not exist. The γ-phase is not observed if the cell volume of the β-phase is close to that of $Ce_{10}S_{14}O$. However, a higher cell volume of the β-phase does not always imply formation of the γ-phase. Under our conditions, the predominant factor is the heating rate.

For dysprosium oxalate, two temperatures were used, 800 and 1000 °C (Table 7). When the heating rate was 5 °C min^{-1}, the pure cubic phase was obtained whatever the temperature.

Table 6 Cerium sulfide obtained at 800 °C by treating the corresponding oxalate as a function of the heating rate and time of treatment

heating rate/°C min^{-1}	0.3	1	5	30	5	5
time/h	1	1	1	1	2	36
observed phases	γ-Ce_2S_3, β-Ce_2S_3 (30%)	γ-Ce_2S_3, β-Ce_2S_3 (40%)	β-Ce_2S_3	β-Ce_2S_3	β-Ce_2S_3	β-Ce_2S_3
a_γ/Å	8.651(2)	8.646(2)				
V_β/Å^3	4857(11)	4890(11)	4865(5)	4669(5)	4902(12)	4872(5)

Table 7 Dysprosium sulfide obtained by treating the corresponding oxalate as a function of the heating rate

T/°C	800	800	1000	1000	1000	1000	1000
heating rate/°C min^{-1}	5	10	5	5	6	7.5	10
time/h	1	1	1	2	1	1	1
observed phases	γ-Dy_2S_3	γ-Dy_2S_3, α-Dy_2S_3 (*ca.* 5%)	γ-Dy_2S_3	γ-Dy_2S_3	α-Dy_2S_3, γ-Dy_2S_3 (10%)	α-Dy_2S_3	α-Dy_2S_3
α_γ/Å	8.313(6)	8.310(3)	8.306(3)	8.310(4)	8.312(4)		
V_α/Å^3					428.3(1)	428.0(6)	428.4(9)

Table 8 Sulfurization of the mixed oxalate $Ce_{1.33}Dy_{0.67}(C_2O_4)_3 \cdot 10H_2O$ as a function of the time of treatment and the heating rate

T/°C	800	800	800	800	800	800	800	900	1000
heating rate/°C min^{-1}	5	10	30	50	5	5	10	10	10
time/h	2	2	2	2	1	5	4	2	2
observed phases	γ-Ce_2S_3, β-Ce_2S_3 (trace)	γ-Ce_2S_3, β-Ce_2S_3 (15%)	γ-Ce_2S_3, β-Ce_2S_3 (25%)	γ-Ce_2S_3, β-Ce_2S_3 (35%)	γ-Ce_2S_3, β-Ce_2S_3 (trace)	γ-Ce_2S_3, β-Ce_2S_3 (trace)	γ-Ce_2S_3, β-Ce_2S_3 (20%)	γ-Ce_2S_3, β-Ce_2S_3 (20%)	α-$CeDyS_3$
a_γ/Å	8.561(7)	8.546(5)	8.537(7)	8.546(7)	8.549(7)	8.553(4)	8.548(4)	8.548(5)	

At higher heating rates, the α-phase begins to appear and, here, the temperature is an important parameter. At $v = 10$ °C min^{-1}, the α-phase is pure at 1000 °C while it appears only in traces at 800 °C. Also at 1000 °C, the nature of the observed phases is also extremely dependent upon the heating rate: the γ-phase is obtained pure at $v = 5$ °C min^{-1} while it is obtained only in traces at 6 °C min^{-1}. Thus, it seems that both heating rate and temperature influence the nature of observed sulfides.

Ternary sulfides. We have studied the effects of temperature and time of treatment on the sulfurization of the mixed-lanthanide (Dy/Ce = 0.50) oxalate. The corresponding results are reported in Table 8. At 800 °C and $v = 5$ °C min^{-1}, the γ-phase is obtained, the β-form being present only in traces. At higher heating rates (from 10 to 50 °C min^{-1}), this latter phase increases but remains the minor component. No significant change in the proportions of the phases is observed as a function of the time of treatment, from 1 to 5 h (at 800 °C and $v = 5$ °C min^{-1}). In contrast, the temperature seems to be a predominant factor: at 1000 °C, the pure α-phase is obtained while a mixture of γ and β phases is observed at 800 and 900 °C.

These results underline that, for a given precursor, the heating rate has a substantial effect on the observed phase with the cubic phase being favoured at low heating rate. Since the time of treatment seems to have no effect on the nature of the phase, it is thus obvious that the nature of the compounds formed at intermediate temperatures (below 800 °C) is of major importance. Our results are in the opposite sense to those obtained by Skrobian *et al.*;[24] this may be related to the use of different precursors. Further work is required to elucidate the reasons for this.

Conclusions

This study clearly shows that, by treating lanthanide oxalates with carbon disulfide vapour, the formation of the corresponding sesquisulfides (the β-form is considered as a sesquisulfide) mainly depends on the treatment conditions (temperature and rate of heating). For a fixed heating rate $v = 5$ °C min, the pure γ-phase is observed for Sm–Ho at 800 °C and for Nd–Dy at 1000 °C. Although the obtained sulfides contained carbon and oxygen, it is the first time that the existence of the γ-form is evident at such a low temperature (800 °C) which is relevant to a soft chemistry process. The formation of the γ-phase of heavy lanthanides such as holmium, yttrium and erbium (impure) is still more surprising and is in contrast to literature data. We can define a range of ionic radius in which the cubic variety is stable under our conditions at 800 °C: $1.015 < r_{Ln^{3+}}/\text{Å} < 1.104$. When the ionic radius of a single lanthanide(III) or the mean radius (r_m) of a mixed lanthanide ($Ce_{2-x}Ln_xS_3$) is between these limits the cubic phase is the stable.

The nature of the rare-earth sesquisulfides is very dependent on the heating rate used. In CS_2 atmosphere, the lower the heating rate, the higher the proportion of the γ-phase. Consequently the phase transitions, which usually depend on the temperature, are not so clearly defined. At a given temperature, the α, β and γ phases, either stable or metastable, may be formed by modifying the nature of precursor and the treatment conditions, principally the heating rate.

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