Thermolysis of lanthanide dithiocarbamate complexes

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ARTICLE INFO

ABSTRACT

Polycrystalline lanthanide sulfide materials were formed at low temperatures using a single-source precursor based on the lanthanide dithiocarbamate complex. The synthesis temperatures are generally lower than standard solid state preparations, avoid toxic sulfurizing gases and provide a convenient route to prepare lanthanide chalcogenide nanoparticles. Depending on the reaction conditions and oxophilicity of the lanthanide, the sulfide material was formed with oxidized products including oxysulfides, oxysulfates and the oxide.

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1. Introduction

The materials formed from lanthanides and oxides and or sulfides are of interest for a wide range of applications from optical (such as phosphors Y_2O_3:Eu, or Y_2O_2S:Eu), to electronic (Ln_2O_3 high κ dielectrics) and catalytic (e.g. CeO_2). In addition to different compositional phases, the sesquisulfides, Ln_2S_3, also exhibit at least three polymorphs (α, β, γ), of which the γ-phase is of particular interest for pigmentation in plastics and paints [1] as well as thermoelectric conversion materials [2]. The mixed-lanthanide γ-$LnLn'S_3$ materials have been found to exhibit impressive variability in structure, as well as optical and magnetic properties [3]. One of the limitations of the lanthanide sulfide materials is the generally high temperatures required for synthesis. Based on recent reports synthetic temperatures can range from as low as 850 °C in the case of samarium sulfides [4] to > 2000 °C in the case of cerium sesquisulfide [5]. In addition, the sesquisulfides, Ln_2S_3 are commonly formed through the sulfurization of the sesquioxides (Ln_2O_3), which involves the use of toxic gases such as hydrogen sulfide or carbon disulfide [6,7]. Other routes include metathesis reactions ($LnCl_3$ and Na_2S_2) [8] or flux methods (for example alkali metal halide) [9] which are not amenable to nanoparticle synthesis.

Our group has been interested in synthesizing nanoparticles of lanthanide chalcogenide materials [10,11], and discovered that lanthanides complexed with dithiocarbamate ligands, $Ln(S_2CNR_2)_3$ Phen (Ln=lanthanide, R=alkyl, Phen=phenanthroline), are great precursors [12]. The complexes are air-stable and easy to prepare, unlike the thiolates previously studied [13–15]. These single source precursors decompose at low temperatures, generally in a single step at temperatures between 250 and 400 °C, and contain an excess of sulfur (the Ln:S ratio is 1:6). As a result these dithiocarbamate complexes provide an interesting opportunity to study the thermodynamically and kinetically stable phases of $Ln_xS_yO_z$ under a range of thermal and atmospheric conditions.

Because the nanoparticles are formed through the thermolysis of the single-sourced precursors in coordinating solvents, a catalog of thermolysis products should facilitate nanoparticle synthesis. We have found that the products of solid state thermolysis is a strong indictor of the phase formed under nanoparticle synthesis. Interestingly, solution thermolysis, particularly in the presence of oleylamine [11] occurs at lower temperatures (e.g. 240 °C for EuS nanoparticles) than the solid state decomposition. Here, we were interested in identifying the most stable phase by thermal decomposition at the lowest temperatures and for the least amount of time required to obtain identifiable X-ray powder diffraction patterns. Two methods of thermolysis were used, sealed tube and vacuum conditions. For select complexes representing early, middle and late lanthanides the effect of temperature and time on the thermolysis products were also investigated. The products formed reflect periodic trends in oxophilicity, as well as differences based on oxidation state stability (divalent metals, Eu, or tetravalent Ce).

2. Experimental section

The lanthanide dithiocarbamate precursors, $Ln(S_2CNEt_2)_3$phen (Ln=La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu,

Et=ethyl), were synthesized using our previously published procedures [12]. The precursors were decomposed using two different methods: thermolysis under vacuum (Method 1) and heating the precursor inside a sealed quartz tube (Method 2). In Method 1, $Ln(S_2CNEt_2)_3$phen was placed in a quartz tube and was heated in a furnace under vacuum, with the organic side products collected in a trap cooled in liquid nitrogen. To obtain a more crystalline product, some products were isolated from the thermolysis and annealed under vacuum. In Method 2 the precursor was loaded in the quartz tube inside a glove box and the system was sealed and heated. In some cases, to obtain a more crystalline product, the solid isolated from this method was annealed in a sealed quartz tube.

Method 1: *Ln*=La, Ce, Pr, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu: Precursors were heated at 900 °C for 5 h; *Ln*=Nd: Precursor was heated at 500 °C for 3 h, 700 °C for 3 h, and 900 °C for 4 h; *Ln*=Eu: Precursor was heated at 500 °C for 3 h, then 700 °C for 3 h.

Method 2: *Ln*=La, Ce, Pr, Sm, Tb, Dy, Tm, Yb, Lu: Precursors were heated at 900 °C for 5 h; *Ln*=Nd: Heated at 500 °C for 8 h, 700 °C for 2 h, 900 °C for 4 h; *Ln*=Gd: Heated at 500 °C for 8 h, 700 °C for 1 h, and 900 °C for 7 h; *Ln*=Ho: Heated at 500 °C for 6 h, 900 °C for 3 h; *Ln*=Er: Heated at 500 °C for 8 h, 700 °C for 1 h, 900 °C for 3 h.

Thermal analysis was performed on an SDT Q600 TA instrument. Simultaneous TGA-DTA data were studied from samples in an alumina pan from 25 to 1000 °C under a N_2 flow of 50 mL/min. The heating rate was initially set at 10 °C/min and was changed to 20 °C/min when the temperature went beyond 600 °C. X-ray powder diffraction patterns were obtained using a Rigaku RAPID Curved IP X-ray powder diffractometer with Cu$K\alpha$ radiation and an image plate detector. Products were identified by referencing known powder patterns using MDI Jade 5.0.

3. Results and discussion

The lanthanide dithiocarbamate tris complexes, $Ln(S_2CNR_2)_3$ Phen, form homologous structures for all the lanthanides. Without exception, the lanthanide exhibits a coordination number of 8, with six *Ln*–S and two *Ln*–N bonds with similar bond angles. The bidentate amine is important for completing the coordination environment of the large lanthanides (although the 6 coordinate tris complex can be formed as well as the tetrakis complex although both are notably less stable) [12]. The *Ln*–S and *Ln*–N bond lengths decrease systematically, reflecting the lanthanide contraction across the series. Based on the spectroscopic covalent parameters of the *Ln*(III)-ligand bonds, such as the nephelauxetic ratio (β), Sinha's parameter (δ), and bonding parameter ($b^{1/2}$) the bonding in these complexes is very ionic [16], although there is increasing covalent character for the heavier lanthanides.

3.1. Thermal analysis

Using TGA-DTA, we evaluated the thermal stability of the $Ln(S_2CNEt_2)_3$phen precursors (representative TGA curves in Fig. 1, all other data can be found in the Supplemental Information). The weight loss occurs in a single step for all the lanthanides, with the exception of cerium (which had two steps). The experimental weight loss for the decomposition of these complexes suggests that the organic component is completely lost leaving only the inorganic core. We occasionally observe phenanthroline solid forming at the cold end of the tube for thermolysis of the lanthanide complexes in sealed tubes [17]. The solid material left after thermal decomposition cannot be definitively identified based on weight loss alone, as the sulfide and oxysulfides are quite close in molecular weight. Generally, it appears the final weight is close
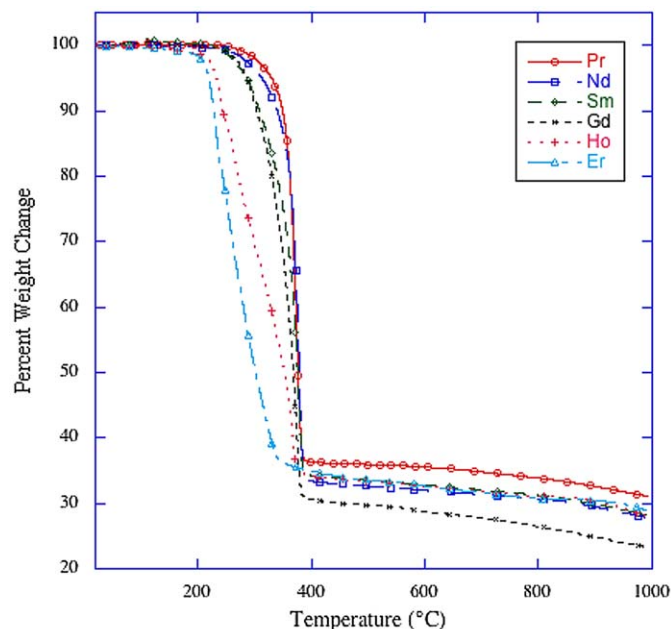

Fig. 1. Thermogravimetric analysis of $Ln(S_2CNEt_2)_3$phen (*Ln*=Pr, Nd, Sm, Gd, Ho, Er).

to Ln_2S_3, but the slow loss of weight above the decomposition temperature suggests that the lanthanide sulfide is slowly converted to the oxide, in agreement with our pyrolysis experiments (vide infra). Cerium is the notable exception with a two-step thermal decomposition, most likely due to the differences in oxidation state stability, resulting in a final product comprised of the oxide phase (CeO_2).

The nature of the ligand appears irrelevant to the thermal stability. For example, changes to the alkyl group (*R*) of the dithiocarbamate ligand, does not alter the decomposition temperature [12]. The primary factor determining the thermal stability is the metal radii. As shown in Fig. 1, the onset of decomposition generally decreases in temperature as the ionic radius decreases across the lanthanide series. This is consistent with the expected increase in lattice energy (or lattice enthalpy) for the smaller lanthanides in ionic solids. In addition, the lanthanide dithiocarbamate complexes have been observed to become progressively less stable with decreasing lanthanide ionic radius [18].

3.2. Precursor thermolysis: Method 1, vacuum

To study the thermal decomposition products of $Ln(S_2CNEt_2)_3$phen (*Ln*=La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) , two thermolysis methods were used to form polycrystalline materials. In the first method a vacuum was used to remove the organic side products, and in the second method the precursors were sealed in an evacuated sealed tube. All products for both methods, using phase identification of the X-ray powder diffraction patterns, are summarized in Table 1. Generally decomposition temperatures of at least 900 °C were required to obtain crystalline, identifiable, X-ray powder diffraction patterns. The exception was Eu, which formed a crystalline material at lower temperatures (~700 °C). Representative PXRD patterns of the products obtained from the decomposition using Method 1 are shown in Fig. 2 of the early lanthanides (Pr, Nd, Sm), Fig. 3 of the middle lanthanides (Gd, Ho, Er), and late lanthanides (Yb, Lu) in Fig. 4. Generally, the products formed using Method 1 contained both γ-Ln_2S_3 and Ln_2O_2S for the early and middle lanthanides, whereas

Table 1
Products from thermal decomposition of precursors using Methods 1 and 2.

Meth.	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
1	OSu	O*	S, OS	S, OS	S, OS	S*	S, OS	OS, O	OS, O	OS	OS	OS	OS, O	OS, O
2	S	S	S	S	S	S*	S	OS	S	S	S	OS	OS	OS

Green S=Sesquisulfide (Ln_2S_3), Green S*=Monosulfide (LnS), Orange OSu=Oxysulfate ($Ln_2O_2SO_4$), Blue OS=Oxysulfide (Ln_2O_2S), Red O=Oxide (Ln_2O_3), Red O*=Oxide (LnO_2).
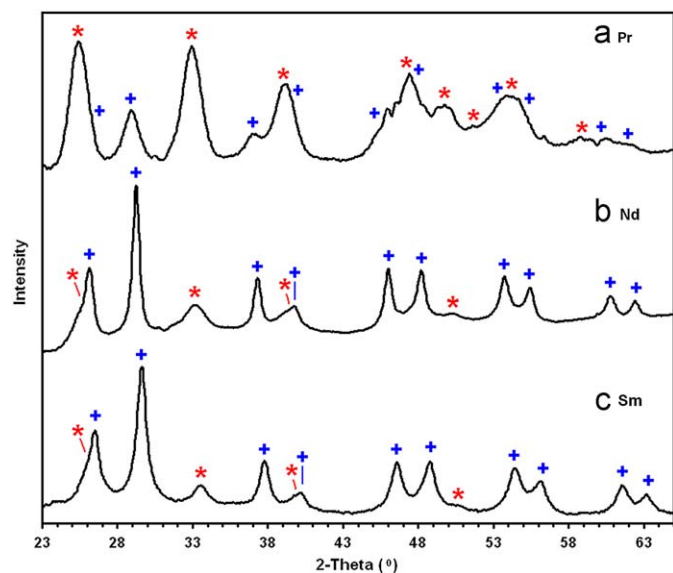

Fig. 2. PXRD pattern of the thermolysis product of $Ln(S_2CNEt_2)_3$phen using Method 1. (a) Ln=Pr; (b) Ln=Nd; (c) Ln=Sm. Peaks marked by the red star correspond to γ-Ln_2S_3 whereas peaks marked with the blue cross match the pattern for Ln_2O_2S. (For interpretation of the references to the color in this figure legend, the reader is referred to the web version of this article.)
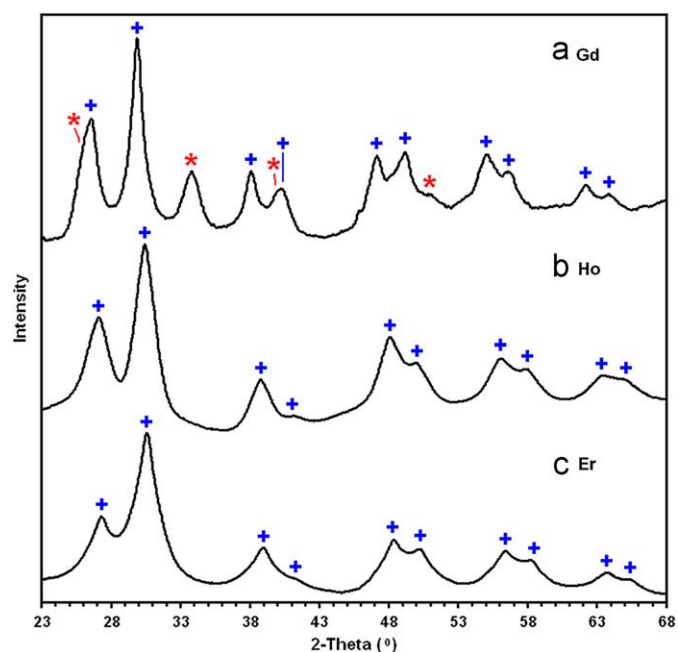

Fig. 3. PXRD pattern of the thermolysis product of $Ln(S_2CNEt_2)_3$phen using Method 1. (a) Ln=Gd; (b) Ln=Ho; (c) Ln=Er. Peaks marked by a blue cross match the pattern for Ln_2O_2S whereas peaks marked by a red star correspond to γ-Ln_2S_3. (For interpretation of the references to the color in this figure legend, the reader is referred to the web version of this article.)

Fig. 4. PXRD pattern of the thermolysis product of $Ln(S_2CNEt_2)_3$phen using Method 1. (a) Ln=Yb; (b) Ln=Lu. Note: blue cross: Ln_2O_2S. (For interpretation of the references to the color in this figure legend, the reader is referred to the web version of this article.)
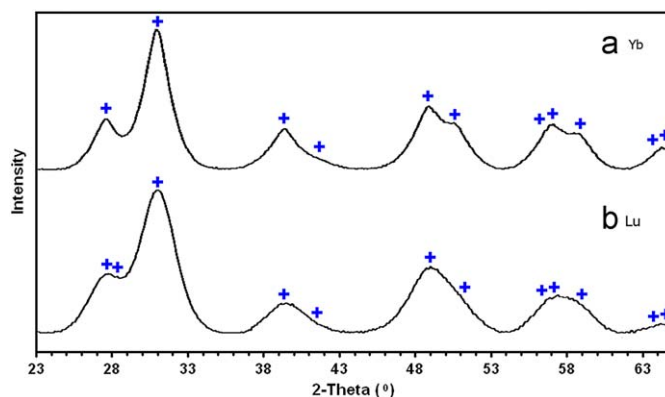
the late lanthanides exhibited a mixture of and Ln_2O_2S and Ln_2O_3. Although modest efforts were made to remove oxygen, the oxophilic lanthanides were able to scavenge oxygen incorporating it to varying degrees under almost all conditions. The early lanthanides, shown in Fig. 2, have the simple trend that the γ-Ln_2S_3 is favored for the largest lanthanide (Pr, element 59) with less amounts of the oxysulfide, and by Sm (element number 62) the oxysulfide (Ln_2O_2S) is dominant with small amounts of the γ-Ln_2S_3. Although Gd (64) still has evidence of the sesquisulfide, elements heavier than Ho have none and the dominant phase is the oxysulfide. The smallest lanthanides also exhibit the sesquioxide (Ln_2O_3). Considering the entire series, clearly oxygen incorporation increases in going from La to Lu. The higher charge densities for the late lanthanides, should result in 'harder' ions, more typical of 'type a' cations [19]. These metal ions have stronger affinity for the 'hard' anion, oxygen. Generally the complex ion stability for class 'a' ions is: $O \gg S > Se, > Te$ [20]. For the majority of lanthanides the ionic radius and oxophilicity determines the phase stability.

The exception to the general trends described above, include lanthanum, cerium and europium; each for a different reason. In the case of lanthanum, the largest of the lanthanides studied, the dominant phase formed was the oxysulfate, $La_2O_2SO_4$. Lanthanide oxysulfides (Ln_2O_2S) are known to oxidize to form the corresponding oxysulfates ($Ln_2O_2SO_4$) in the presence of oxygen [21]. The oxysulfates thermally decompose to form the corresponding sesquioxides at temperatures above 1200 °C [22]. The oxidation of the oxysulfide is exothermic, but quite slow and the rate decreases as the ionic radii decreases. In addition, particle size and crystallinity were other important factors in the rate of oxidation of the lanthanide sulfides [23]. Generally, the range of thermal stability of the oxysulfate decreases with decreasing radii, which is the likely reason why the oxysulfate was observed only for the largest lanthanide, La.

Cerium in many ways is distinct from all the other lanthanides in these experiments. Cerium has the lowest fourth ionization of the lanthanides, and has the most stable tetravalent oxidation state. This lanthanide is the most oxophilic, and the ease of oxidation of Ce^{3+}–Ce^{4+}, results in the formation of CeO_2. The TGA exhibited two steps, associated with first the loss of ligands and secondly oxidation of cerium to produce CeO_2.

The final exception, another redox active lanthanide, was europium. The europium dithiocarbamate precursor thermally decomposed to form the monochalcogenide, EuS at all temperatures. It was the only lanthanide with a stable divalent state to do so although Sm, Tm Yb also have stable Ln(II) oxidation states.

Generally, lanthanide thiolate complexes thermally decompose to produce LnS for divalent precursors and Ln_2S_3 from the trivalent precursors. The exception to this observation are the europium thiolates, which tend to result in EuS, whether the precursor oxidation state is divalent or trivalent. This is consistent with europium having the most stable divalent state, and reflected in the phase diagram of the chalcogenides which have the largest temperature and composition range of stability of the mono-chalcogenide [24].

3.3. Precursor thermolysis: Method 2, sealed

Heating the precursor complexes in a pre-evacuated sealed quartz tube (Method 2) also gave black solids. For precursors where Ln=Pr, Nd, Sm and Gd, a crystalline product was achieved only after annealing between 700 and 900 °C. Method 2 successfully yielded the sesquisulfides for the lanthanides up to Er. The fact that only the smallest lanthanides (Tm–Lu) formed the oxysulfides is consistent with the previously observed trend in increasing oxophilicity of the smallest lanthanides. It in unclear why the Tb compound formed the oxysulfide while the Dy–Er formed the sesquisulfide.

The primary difference between Methods 1 and 2, was whether the organic side products were removed or left in contact with inorganic material. In Method 2, the precursor was decomposed inside a sealed tube, resulting in continued reaction between the inorganic material and the sulfurous organic oil. The organic side products are both reducing and provide an additional source of sulfur. Thus, it is not surprising that pure Ln_2S_3 sesquisulfides were formed using Method 2; the carbothermal treatment would remove any oxide as CO_2 and the excess sulfur would ensure complete sulfurization. Again, the only exception to this was europium which again formed EuS. Generally, the resulting PXRD patterns from Method 2 were less crystalline than the counterpart formed from Method 1, as seen in Figs. 6–8. The presence of the amorphous organic materials may influence the annealing process or slow the rate of crystallization.

The sesquisulfides of lanthanides are known to exist in a variety of polymorphic forms, whose stability depends on the temperature and the lanthanide ionic radius [25]. Examination of the PXRD patterns of
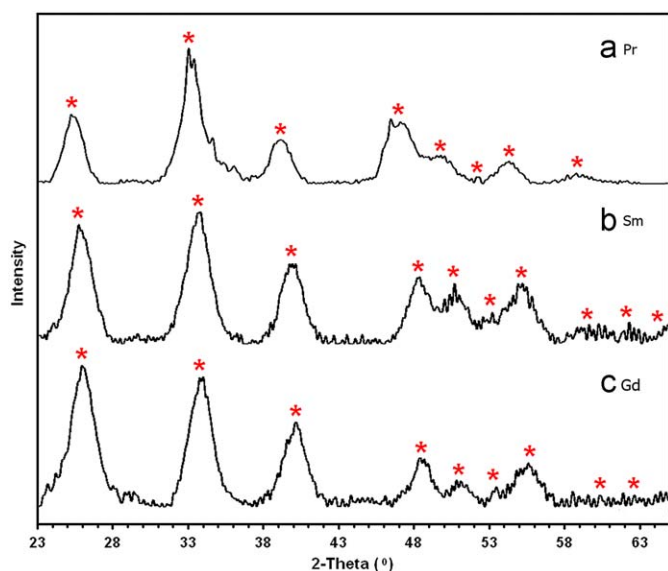

Fig. 6. PXRD pattern of the thermolysis product of La(S_2CNEt_2)$_3$phen (a) Using Method 1. (b) Using Method 2. Note: red star: γ-La$_2$S$_3$; green dot: La$_2$O$_2$SO$_4$. (For interpretation of the references to the color in this figure legend, the reader is referred to the web version of this article.)
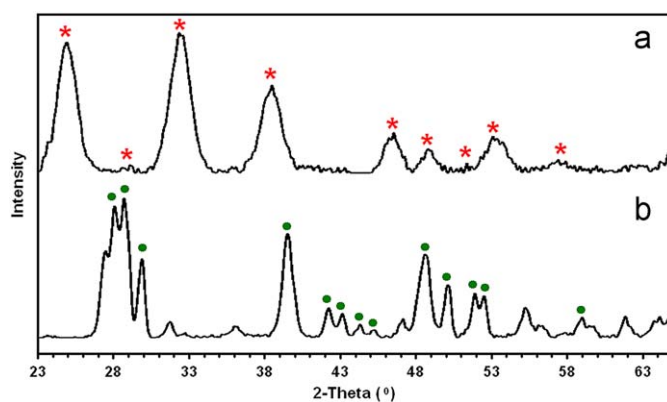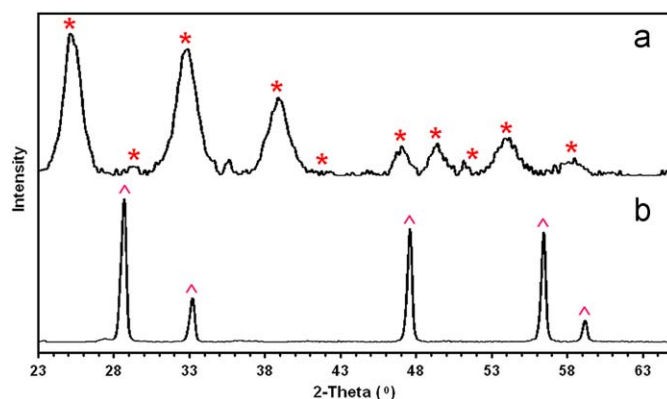

Fig. 7. PXRD pattern of the thermolysis product of Ce(S_2CNEt_2)$_3$phen (a) Using Method 1. (b) Using Method 2. Note: red star: γ-Ce$_2$S$_3$; pink carat: CeO$_2$. (For interpretation of the references to the color in this figure legend, the reader is referred to the web version of this article.)

Fig. 8. PXRD pattern of the thermolysis product of Dy(S_2CNEt_2)$_3$phen (a) Using Method 1. (b) Using Method 2. Note: red lines: Dy$_2$S$_3$; blue lines: Dy$_2$O$_2$S; purple lines: Dy$_2$O$_3$. (For interpretation of the references to the color in this figure legend, the reader is referred to the web version of this article.)
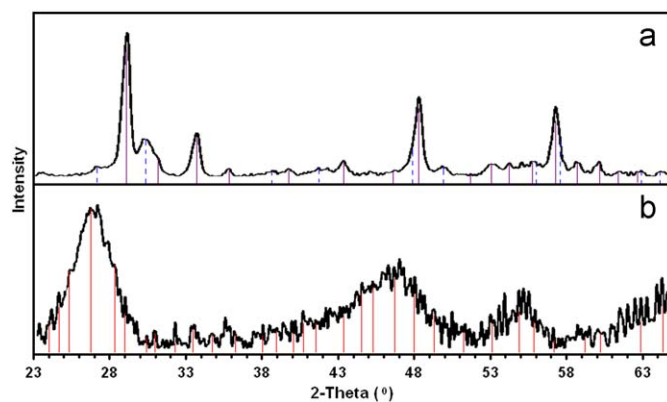
the materials obtained from the decomposition of precursors Ln(S_2CNEt_2)$_3$phen (Ln=Pr, Nd, Sm, Gd) using Method 2 revealed that the sesquisulfides formed are of the γ type (see Fig. 5), which is the known stable phase for the lighter lanthanides (La–Tb) at high temperatures. This phase has a cubic Th$_3$P$_4$ defect structure, where the lanthanides are octa coordinate. Among the various forms of Ln_2S_3, the γ-phase has been the most widely studied because of their

Fig. 5. PXRD pattern of the thermolysis product of Ln(S_2CNEt_2)$_3$phen using Method 2 (a) Ln=Pr; (b) Ln=Sm; (c) Ln=Gd. Note: red star: γ-Ln_2S_3. (For interpretation of the references to the color in this figure legend, the reader is referred to the web version of this article.)

potential for use as pigments for plastics and paints, thermoelectric converters, and optical materials in IR windows, lasers and magneto-optical devices [26]. In previous studies, γ-Ln_2S_3 of the light lanthanides are generally prepared at temperatures above 1000 °C [6]. Below this temperature, they usually exist in either the orthorhombic α-phase or the tetragonal β-form. Romero et al. have been the first to successfully obtain the γ-phase at relatively low temperatures (800–1000 °C), and this was done by treating lanthanide oxalates with CS_2 at a fixed heating rate of 5 °C/min [27]. This method, however, requires the use of CS_2, which, despite being a powerful deoxygenating and sulfurizing agent, is highly flammable and toxic. Thus, the single-source precursor approach, which is used in this study, provides a simpler and less hazardous way of producing γ-Ln_2S_3 at relatively low temperatures (700–900 °C).

On the other hand, the sesquisulfides obtained from the thermolysis of the Ho and Er precursors are of the monoclinic δ type. In δ-Ln_2S_3, half of the lanthanides have 6-fold coordination while the other half are 7-coordinate [28]. This form is characteristic of the sesquisulfides of Dy–Tm. The relatively smaller size of these lanthanides favors lower coordination, which explains the greater stability of the δ-phase relative to the γ-phase. Complete conversion of the monoclinic δ-phase to the cubic γ-form has been previously observed, but this requires high-temperature and high-pressure treatment [29]. In the case of Dy, complete transformation has been attained at 1200 °C and 70 kbar. For Ho–Yb, complete transition occurred at 2000 °C and 77 kbar.

4. Conclusion

Thermal decomposition of a single-source lanthanide dithiocarbamate precursor was successfully employed to obtain lanthanide chalcogenide materials. Based on the increasing oxophilicity of the lanthanides across the series, and the temperature and atmosphere in which they are decomposed, sulfides, oxysulfides, oxysulfates, and oxides can result. Although the lanthanides are very similar, the unique redox properties of Ce and Eu resulted in exceptions to the overall trends in phase formation. The utility of the dithiocarbamate precursors demand careful oxygen exclusion to form exclusively the sulfide materials.

Acknowledgment

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2009.10.003.

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