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# Lanthanide polysulfides at high pressures

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**Abstract**

High pressure behavior of selected stoichiometric lanthanide disulfides and sesquisulfides is studied in a diamond cell by X-ray diffraction, Raman spectroscopy, and optical reflectivity. Upon compression to 20 GPa, there occurs a reversible phase transition in layered $\alpha'$-$LnS_2$ (Ln: La–Nd) rare earth disulfides ($P2_1/b$, $C_{2h}^5$, $Z=4$) with the distorted anti-$Fe_2As$ structure (the PbFCl type, $P4/nmm$, $D_{4h}^7$, $Z=2$) to higher symmetry superstructures of the parent anti-$Fe_2As$ type. This transformation at about 5 GPa for $\alpha'$-$LaS_2$, $\alpha'$-$CeS_2$, and $\alpha'$-$PrS_2$, and at about 8 GPa for $\alpha'$-$NdS_2$ is associated with changes in the scheme of direct optical transitions. $\gamma$-$Gd_2S_3$ with the defect $Th_3P_4$ structure ($I\bar{4}3d$, $Z=4$) remains stable to at least 30 GPa. There occurs a reversible phase transition in $\varepsilon$-$Lu_2S_3$ ($Lu_2S_3$-I) with the corundum structure ($R\bar{3}c$) to the $Th_3P_4$ type ($I\bar{4}3d$) above 5.0 GPa ($Lu_2S_3$-V or $\gamma$-$Lu_2S_3$). There is no evidence for the presence of intermediate phases of the $Tm_2S_3$-II ($Lu_2S_3$-II, $P2_1/m$), $U_2S_3$ ($Lu_2S_3$-III, $Pnma$), and $NdYbS_3$ ($Lu_2S_3$-IV, $Pnma$) types up to 20 GPa. All the compounds remain semiconducting in the entire pressure range covered in this study. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Semiconductors; Crystal structure and symmetry; Phase transitions; High pressure

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## 1. Introduction

Rare-earth disulfides and sesquisulfides are refractory compounds and wide-gap high-resistivity semiconductors. They have potential application as far-infrared transmitting materials, lasers, phosphors, scintillators, and magneto-optical devices [1–3]. These compounds are also precursors for several crystalline and amorphous systems. Much effort has been concentrated on techniques to process them and to tune their optical and electronic properties.

In this study, the effect of pressure on the structures and optical properties of lanthanide disulfides and sesquisulfides is examined for selected compounds using X-ray diffraction, Raman spectroscopy, and optical reflectivity measurements in a diamond anvil cell. More details on the structural transitions, along with the description of sample preparations and experimental procedures, are presented elsewhere [4–6]. The optical reflectivity spectra presented show a correlation between structural and electronic properties as these compounds undergo pressure-induced phase transitions. Several quenchable polymorphic modifications of these compounds, depending on temperature and pressure conditions of synthesis, have already been reported. However, these studies do not give any direct (in situ) evidence about the actual transformations and phase equilibria. Diamond cell studies provide invaluable information on the phase stability and occurrence of fully reversible phase transformations.

## 2. Phase transformations in lanthanide disulfides: Raman studies

The ideal structure of rare earth dichalcogenides $LnX_2$, $Ln^{3+}X^{2-}(X_2^{2-})_{1/2}$ (Ln: La–Lu; X: S, Se, Te), is of the anti-$Fe_2As$ type ($P4/nmm$, $D_{4h}^7$, $Z=2$, $a_0 \approx 4$ Å, $c_0 \approx 8$ Å). In this structure, layers of five chalcogen atoms in the basal face-centered square plane (the Flahaut plane) are separated by two slabs of alternating $Ln^{3+}$ (the 9-fold coordination) and $X^{2-}$ ions. All the $LnX_2$ compounds are distorted from this due to the formation of X–X pairs within the basal planes [7]. This distortion gives rise to a number of pseudo-cubic, tetragonal, orthorhombic, and monoclinic ($\beta \approx 90°$) anti-$Fe_2As$ superstructures. Strong covalent binding in the S–S dimers accounts for semiconducting properties of these materials.

Different polymorphs of stoichiometric light rare earth disulfides (La–Nd) are obtained at ambient pressure but variable temperatures [8–11]: $\alpha$ ($\alpha'$) ($P2_1/b$, $C_{2h}^5$, $Z=4$), $\beta$

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(*Pnma*, $D_{2h}^{16}$, $Z=8$), $\gamma$ (*P4*/*nmm*, $D_{4h}^{7}$, $Z=2$). Preparation of stoichiometric heavier rare earth disulfides requires high pressure techniques [12]. Depending on the conditions of the reaction of the respective elements, pseudo-cubic or tetragonal products are recovered to ambient conditions. The actual pressure necessary to synthesize stoichiometric compounds increases along the Sm–Lu rare earth series.

The first-order Raman spectra of $\alpha'$-$LnS_2$ (Ln: La–Nd) at and near ambient conditions are similar, the only differences being in the absolute positions of the respective bands (the selection rules: $\Gamma=9A_g+9B_g+8A_u+7B_u$, where the $A_g$ and $B_g$ modes are Raman active, and the $A_u$ and $B_u$ modes are infrared active) [4]. Fig. 1 shows representative Raman spectra of $NdS_2$ under pressure. The strongest bands at about 400–430 $cm^{-1}$ are well resolved at lowest pressures for all the compounds. Their scattering intensity appears predominantly for parallel polarization vectors of incident and scattered photons ($E_i$ II $E_s$) [13]. All these compounds contain the $(S–S)^{2-}$ ions as a common structural feature according to the formula $Ln^{3+}S^{2-}(S_2^{2-})_{1/2}$. Hence, the strong Raman bands are attributed to the S–S stretching vibration of the $(S–S)^{2-}$ ions ($A_g+B_g$). Upon compression, these two bands merge and the higher frequency components have negative pressure shifts. This band convergence occurs at about 5 GPa for $\alpha'$-$LaS_2$, $\alpha'$-$CeS_2$, and $\alpha'$-$PrS_2$, and at about 8 GPa for $\alpha'$-$NdS_2$. In addition to this, in every case a new band appears at about 430 $cm^{-1}$ at pressures above 8 GPa. Upon decompression to ambient conditions, all the spectral changes are reversible with a hysteresis of about 3–4 GPa at each case.

Analysis of the Raman spectra of the $LnS_2$ compounds with different superstructures [11] reveals the absence of splitting of the strongest band at about 400–430 $cm^{-1}$ in the pseudo-cubic and tetragonal polymorphs at ambient conditions. The experimental observations presented here can be interpreted as an evidence for sluggish pressure-induced phase transitions in layered $\alpha'$-$LnS_2$ (Ln: La–Nd) rare earth disulfides ($P2_1/b$, $C_{2h}^{5}$, $Z=4$). Upon compression, the most intense Raman bands merge indicating the ascence of symmetry for the anti-$Fe_2As$ superstructure. The mechanism for this structural change can be envisioned as a tendency of the 9-fold polyhedra around the $Ln^{3+}$ ions to become more symmetric within the anti-$Fe_2As$ type, i.e. a tendency towards the equivalency of the four Ln–S basal and four, out of five, Ln–S non-basal bonds. From the lack of drastic changes in the number of the observed Raman bands at the respective pressures, it could be argued that the number of the molecular units does not change ($Z=4$) and the resulting high pressure structure is a pseudo-cubic or tetragonal anti-$Fe_2As$ superstructure.

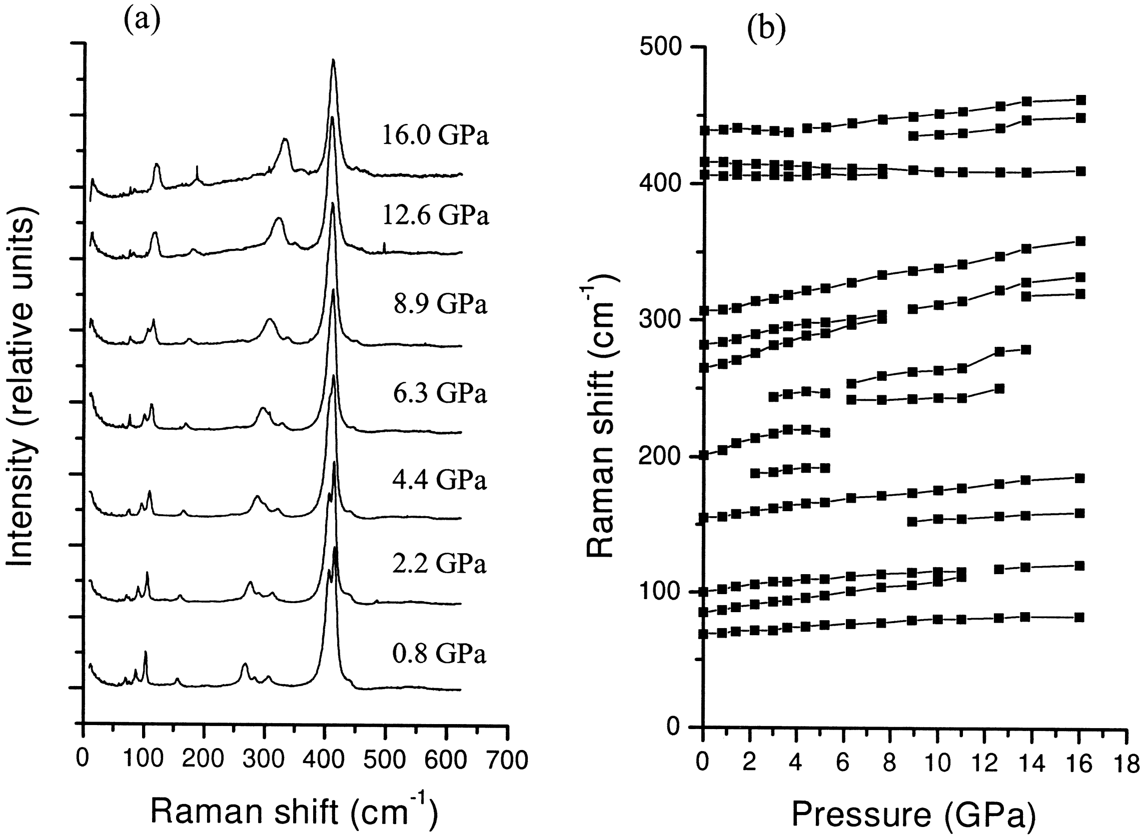

Fig. 1. Raman spectra upon compression (a) and pressure dependence of the observed Raman frequencies (b) in $NdS_2$. All spectra are vertically offset for clarity.

## 3. Phase transformations in lanthanide sesquisulfides: X-ray diffraction studies

Rare earth sesquisulfides $Ln_2S_3$ in the series Ln = La–Dy have three polymorphs at atmospheric pressure [14,15]. The high temperature $\gamma$ phases have a lattice of the $Th_3P_4$ type ($I\bar{4}3d$, $Z=4$), with 8-fold coordinated cations randomly distributed over available sites, $Ln_{2.67\otimes 0.33}S_4$ ($\otimes_{0.33}$ is the number of vacancies). Heavier rare earth sesquisulfides (Ln = Ho–Lu) have six different structural types, depending on cation radii and coordination numbers, and temperature and pressure conditions [14,15]. In these materials, the coordination numbers of the cations vary from six to eight and the higher coordinated polymorphs are obtained at high pressures. At ambient conditions, $Lu_2S_3$ takes the corundum structure ($R\bar{3}c$) with 6-fold coordinated $Lu^{3+}$ cations ($\varepsilon$-$Lu_2S_3$ or $Lu_2S_3$-I). Other polymorphs with this composition are synthesized at high pressures and high temperatures [14,15]. The $Lu_2S_3$-II phase of the $Tm_2S_3$-II type ($P2_1/m$, coordination numbers of the cations are 8, 7, and 6) is obtained at about 1.0–3.0 GPa and 1273 K. The $Lu_2S_3$-III modification with the $U_2S_3$ structure (*Pnma*, coordination numbers 7 and 7+1) is recovered from somewhat higher pressures, but approximately the same temperatures. The $Lu_2S_3$-IV variant of the $NdYbS_3$ type is found at about 3.0 GPa and at temperatures above 1573 K (*Pnma*, coordination numbers 8 and 6).

All the previous reports on the high pressure synthesis of the lanthanide sesquisulfides have dealt with the recovered samples, i.e. metastable compounds at atmospheric conditions [14,15]. In this respect, these studies do not provide any direct (in situ) evidence about the actual transformations and phase equilibria. The corundum→thorium phosphide transition for $Ln_2S_3$ is postulated based on the structural considerations [5,6]. $\gamma$-$Ln_2S_3$ compounds have the smallest reduced volumes and the highest coordination of the cations at ambient conditions, so that all the other polymorphs are expected to transform to the $Th_3P_4$ structure at high pressures.

Fig. 2 displays diffraction patterns of $Lu_2S_3$ up to 23.0 GPa at room temperature. The diffractograms collected above about 5 GPa can be indexed with the cubic cell of the $Th_3P_4$ type ($I\bar{4}3d$) [5]. There is no indication in the patterns for the presence of any intermediate phases

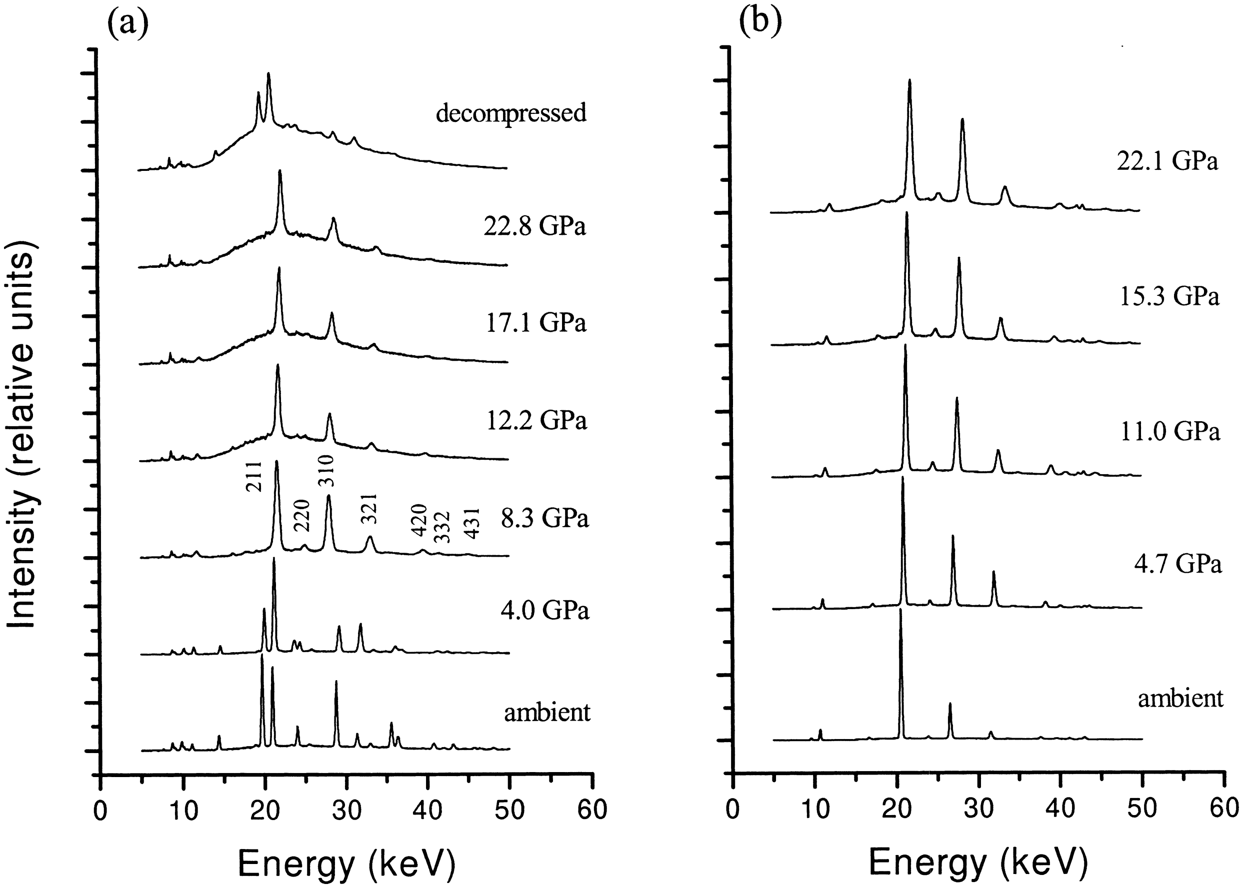

Fig. 2. Energy-dispersive X-ray diffraction patterns of $Lu_2S_3$ (a) and $\gamma$-$Gd_2S_3$ (b) as a function of pressure ($E^*d=70.584\pm0.072$ keV Å). Miller indices are given for the $Th_3P_4$-type phase of $Lu_2S_3$ at 8.3 GPa ($\gamma$-$Lu_2S_3$: $I\bar{4}3d$, $a=7.9957\pm0.0026$ Å, $V=511.18\pm0.50$ Å$^3$). All patterns are vertically offset for clarity.

between the corundum and $Th_3P_4$ types. The data of this study show that ε-$Lu_2S_3$ with the corundum structure at atmospheric conditions ($Lu_2S_3$-I) does undergo a phase transition into the $Th_3P_4$ structure above 5.3 GPa ($Lu_2S_3$-V or γ-$Lu_2S_3$). This fully reversible transition (ε↔γ) occurs at room temperature and does not involve any intermediates with cationic coordination numbers between six and eight ($Lu_2S_3$-II, $Lu_2S_3$-III, $Lu_2S_3$-IV). This suggests that the occurrence of the $Tm_2S_3$-II ($P2_1/m$), $U_2S_3$ (*Pnma*), and $NdYbS_3$ (*Pnma*) types does require high temperatures at high pressures.

The question of stability and further pressure-induced structural and electronic transformations in γ group of rare earth sesquisulfides is still open. γ-$Gd_2S_3$ occurs towards the end of the series of the $Th_3P_4$-structured rare earth sesquisulfides that can be obtained using simple synthesis methods [16] and does not require high pressure [14,15] or attrition milling [17] techniques of preparation. As such, it could serve as a model compound for the entire lanthanide series at high pressure conditions. Combined X-ray diffraction (Fig. 2) and Raman spectroscopy data [6] provide the evidence that there is no structural transition in γ-$Gd_2S_3$ upon compression to 30 GPa. One of the mechanisms for a possible structural change is an increase of coordination around the gadolinium atoms. This would be a driving force to achieve a higher density phase. The stability of γ-$Gd_2S_3$ at high pressures (at least to 30 GPa) suggests that it would not be the case for the entire sesquisulfide group and that the 8-fold cation coordination is the maximum one for this stoichiometry.

## 4. Optical properties

The calculations of the electronic structure in $LnS_2$ with the linear muffin-tin orbital method (LMTO) [18] reveal that the states near the bottom of the conduction band are formed mainly by the 5*d* orbitals of the lanthanum atoms, but there are also considerable (up to 30%) admixtures of the 4*f* orbitals. The top of the valence band is formed by antibonding (relative to the S–S interaction) combinations of the π bonds (parallel to the Flahaut layers) in the S–S dimers. The calculated band gap of 0.95 eV corresponds to indirect transitions Γ–R, R–X, or M–Γ. The measured gaps in α-$LnS_2$ are about 2–2.5 eV for direct transitions and 2 eV for indirect transitions.

Fig. 3 shows optical reflectivity spectra of $NdS_2$ upon compression. The red shift of the high energy reflectivity edge indicates that the lowest energy direct interband transitions shift towards lower energies. The reflectivity in the low energy infrared region does not increase due to free carriers, as a result of a transition (or a tendency towards it) into a metallic state. The reflectance spectra suggest that the oscillator strength just above the band gap due to the direct transitions decreases significantly with increasing pressure up to about 9 GPa. At higher pressures, the optical edge broadens and the reflectivity at high energies rises. This would be related to a new scheme of direct optical transitions at the higher symmetry anti-$Fe_2As$ superstructure.

The fundamental optical band gaps in the γ-$Ln_2S_3$ compounds originate from the separation between the

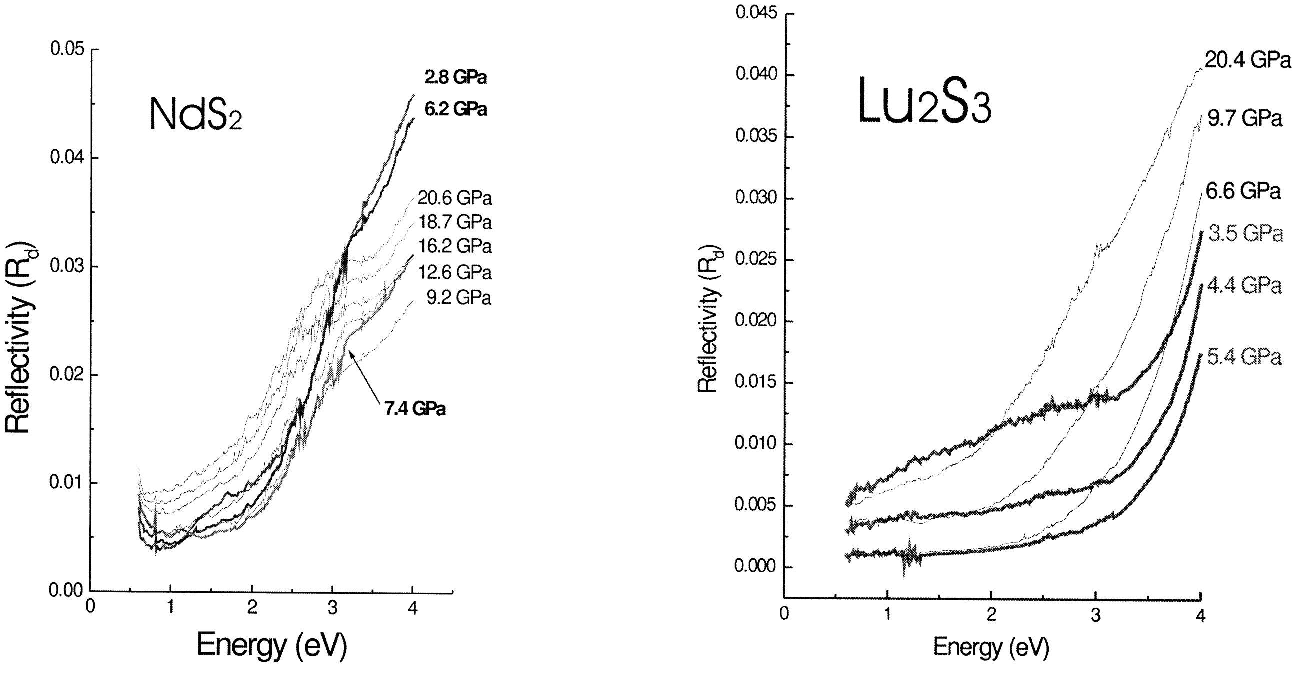

Fig. 3. Optical reflectivity spectra of $NdS_2$ and $Lu_2S_3$ at high pressures. The reflectivity $R_d$ is measured at the diamond–sample interface. There is no vertical offset of the spectra.

3*p*(S) valence band at the M point and the 5*d*(Ln) conduction band at the Γ point of the Brillouin zone [6]. Optical reflectivity spectra in γ-$Gd_2S_3$ up to 20 GPa show a red shift of the lowest energy direct interband transitions. At higher pressures, broadening of the reflectivity spectral features is associated with a loss of Raman intensity as a result of a possible transformation in the electronic structure. The optical reflectivity spectra in $Lu_2S_3$ at high pressures are shown in Fig. 3. At atmospheric pressure, the optical absorption edge for ε-$Lu_2S_3$ with a direct band gap is 3.18 eV [19]. The blue-to-red change in the shift of the high energy reflectivity edge is well correlated with the corundum-thorium phosphide structural phase transition and corresponds to a major change in the electronic structure in this material. Similarly to γ-$Gd_2S_3$, there is no evidence for the increase of reflectivity in the low energy infrared region in $Lu_2S_3$ due to an emergence of free carriers.

## 5. Summary

The observations of this study show that the corundum type of lanthanide sesquisulfides reversibly converge into the non-centrosymmetric structure of thorium phosphide at high pressures ($\epsilon \leftrightarrow \gamma$). Such transformations are not known yet for any oxide analogues of these compounds. Additionally, γ-$Ln_2S_3$ compounds, which can be prepared at ambient pressure, are stable at least to 30 GPa. It implies that the 8-fold cation coordination in the lanthanide sesquisulfide group would be the maximum one for this stoichiometry, unlike the 9-fold one in stoichiometric lanthanide disulfides with the anti-$Fe_2As$ structure. It would mean that in complex crystalline and amorphous systems containing these compounds as precursors, the coordination changes and local symmetry around the lanthanide atoms under pressure would proceed as described here, i.e. depending on the lanthanide:sulfur ratio the maximum coordination would be 8 or 9. It is worth noticing that upon compression, rare earth sesqui- and disulfides remain semiconducting.

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