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Syntheses, structure, magnetism, and optical properties of the interlanthanide sulfides δ-$Ln_{2-x}Lu_xS_3$ (Ln = Ce, Pr, Nd)

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Abstract

δ-$Ln_{2-x}Lu_xS_3$ (Ln = Ce, Pr, Nd; $x = 0.67$–0.71) compounds have been synthesized through the reaction of elemental rare-earth metals and S using a Sb_2S_3 flux at 1000 °C. These compounds are isotypic with $CeTmS_3$, which has a complex three-dimensional structure. It includes four larger Ln^{3+} sites in eight- and nine-coordinate environments, two disordered seven-coordinate Ln^{3+}/Lu^{3+} positions, and two six-coordinate Lu^{3+} ions. The structure is constructed from one-dimensional chains of LnS_n ($n = 6$–9) polyhedra that extend along the b-axis. These polyhedra share faces or edges with two neighbors within the chains, while in the [ac] plane they share edges and corners with other chains. Least square refinements gave rise to the formulas of δ-$Ce_{1.30}Lu_{0.70}S_3$, δ-$Pr_{1.29}Lu_{0.71}S_3$ and δ-$Nd_{1.33}Lu_{0.67}S_3$, which are consistent with the EDX analysis and magnetic susceptibility data. δ-$Ln_{2-x}Lu_xS_3$ (Ln = Ce, Pr, Nd; $x = 0.67$–0.71) show no evidence of magnetic ordering down to 5 K. Optical properties measurements show that the band gaps for δ-$Ce_{1.30}Lu_{0.70}S_3$, δ-$Pr_{1.29}Lu_{0.71}S_3$, and δ-$Nd_{1.33}Lu_{0.67}S_3$ are 1.25, 1.38, and 1.50 eV, respectively. *Crystallographic data*: δ-$Ce_{1.30}Lu_{0.70}S_3$, monoclinic, space group $P2_1/m$, $a = 11.0186(7)$, $b = 3.9796(3)$, $c = 21.6562(15)$ Å, $\beta = 101.6860(10)$, $V = 929.93(11)$, $Z = 8$; δ-$Pr_{1.29}Lu_{0.71}S_3$, monoclinic, space group $P2_1/m$, $a = 10.9623(10)$, $b = 3.9497(4)$, $c = 21.5165(19)$ Å, $\beta = 101.579(2)$, $V = 912.66(15)$, $Z = 8$; δ-$Nd_{1.33}Lu_{0.67}S_3$, monoclinic, space group $P2_1/m$, $a = 10.9553(7)$, $b = 3.9419(3)$, $c = 21.4920(15)$ Å, $\beta = 101.5080(10)$, $V = 909.47(11)$, $Z = 8$.

Keywords: Interlanthanide sulfide; Mixed-lanthanide sulfide; Magnetic properties of lanthanide sulfides

1. Introduction

Ternary interlanthanide chalcogenides display a wide variety of structures that can possess both ordered and disordered Ln^{3+} sites [1–14]. The ordering of two different Ln^{3+} cations over two or more crystallographic sites can be achieved by maximizing the difference in the size of the Ln^{3+} ions. Typical examples of ordered phases include α-LnLn′S_3 ($GdFeO_3$-type [15]) [1–4], β-LnLn′Q_3 (Q = S, Se) ($UFeS_3$-type [16]) [3,5,6], and γ-LnLn′S_3 [7]. In these compounds, there are sharp demarcations in coordination numbers and bond distances between the larger ions and smaller ions, which inhibit the disordering of two lanthanides. In contrast, mixed site occupancies are found in disordered structures, e.g. F-Ln_2S_3 ($CeYb_3S_6$ [9]) [17,18], $CeTmS_3$ [10], and Y_5S_7 ($Sc_2Er_3S_7$ [11]) [19]. When the difference in size between the two Ln^{3+} ions becomes too small, disorder is unavoidable owing to the strong similarities in the structural chemistry of lanthanides. This is best represented by F-Ln_2S_3-type compounds, which contain an eight-coordinate environment for larger Ln^{3+} ion (A), a seven-coordinate intermediate site (B), and two six-coordinate octahedral sites for the smaller Ln^{3+} ion (C). In case of F-$GdLu_3S_6$, the position B is occupied by both metal ions [9]. For F-Er_3ScS_6, both C sites are disordered [8].

In addition to the remarkable structural flexibility of mixed-lanthanide sulfides that gives rise to a myriad of

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structure types, these compounds also display important physical properties including tunable band gaps. In an effort to understand the structure–property relationships in interlanthanide chalcogenides, we present the preparation, structure determination, magnetism, and optical properties of the partially disordered δ-$Ln_{2-x}Lu_xS_3$ (Ln = Ce, Pr, Nd; $x = 0.67$–0.71) ($CeTmS_3$-type) compounds.

2. Experimental

2.1. Starting materials

Ce (99.9%, Alfa-Aesar), Pr (99.9%, Alfa-Aesar), Nd (99.9%, Alfa-Aesar), Lu (99.9%, Alfa-Aesar), S (99.5%, Alfa-Aesar), and Sb (99.5%, Alfa-Aesar) were used as received. The Sb_2S_3 flux was prepared from the direct reaction of the elements in sealed fused-silica ampoules at 850 °C.

2.2. Syntheses of δ-$Ln_{2-x}Lu_xS_3$ (Ln = Ce, Pr, Nd; $x = 0.67$–0.71)

Reaction mixtures included 0.2000 g of Ln, Lu, S, and Sb_2S_3 in a ratio of 1:1:3:0.5 mmol. They were loaded into fused-silica ampoules in an argon-filled glovebox. The ampoules were sealed under vacuum and heated in the following profile using a programmable tube furnace: 2 °C/min to 500 °C (held for 1 h), 0.5 °C/min to 1000 °C (held for 5 d), 0.04 °C/min to 550 °C (held for 2 d), and 0.5 °C/min to 24 °C. High yields of black crystals of δ-$Ce_{1.30}Lu_{0.70}S_3$ and dark red crystals of δ-$Pr_{1.29}Lu_{0.71}S_3$ and δ-$Nd_{1.33}Lu_{0.67}S_3$ were isolated manually. Powder X-ray diffraction measurements were used to confirm phase purity by comparing the powder patterns calculated from the single-crystal X-ray structures with the experimental data. Semi-quantitative SEM/EDX analyses were performed using a JEOL 840/Link Isis or JEOL JSM-7000F instruments. Ln, Lu, and S percentages were calibrated against standards. Sb was not detected in the crystals. The Ln:Lu:S ratios were determined to be approximately 2:1:4.5 from EDX analyses.

2.3. Crystallographic studies

Single crystals of δ-$Ln_{2-x}Lu_xS_3$ (Ln = Ce, Pr, Nd; $x = 0.67$–0.71) were mounted on glass fibers with epoxy and optically aligned on a Bruker APEX single-crystal X-ray diffractometer using a digital camera. Initial intensity measurements were performed using graphite monochromated MoK_α ($\lambda = 0.71073$ Å) radiation from a sealed tube and monocapillary collimator. SMART (v 5.624) was used for preliminary determination of the cell constants and data collection control. The intensities of reflections of a sphere were collected by a combination of three sets of exposures (frames). Each set had a different ϕ angle for the crystal and each exposure covered a range of 0.3° in ω. A total of 1800 frames were collected with exposure times per frame of 10 or 20 s depending on the crystal.

For δ-$Ln_{2-x}Lu_xS_3$ (Ln = Ce, Pr, Nd; $x = 0.67$–0.71), determination of integrated intensities and global refinement was performed with the Bruker SAINT (v 6.02) software package using a narrow-frame integration algorithm. These data were treated first with a face-indexed numerical absorption correction using XPREP [20], followed by a semi-empirical absorption correction using SADABS [21]. The program suite SHELXTL (v 6.12) was used for space group determination (XPREP), direct methods structure solution (XS), and least-squares refinement (XL) [20]. The final refinements included anisotropic displacement parameters for all atoms and secondary extinction. Some crystallographic details are given in Table 1. Atomic coordinates and equivalent isotropic displacement parameters for δ-$Ln_{2-x}Lu_xS_3$ (Ln = Ce, Pr, Nd; $x = 0.67$–0.71) are given in Tables 2–4. Additional crystallographic details can be found in the Supporting Information.

The structure of $CeTmS_3$ was previously determined to be ordered, with four eight-coordinate Ce^{3+} ions, two seven-coordinate Tm^{3+} and two six-coordinate Tm^{3+} ions [10]. However, elemental analysis for δ-$Ln_{2-x}Lu_xS_3$ (Ln = Ce, Pr, Nd; $x = 0.67$–0.71) indicated the ratio of Ln^{3+}:Lu^{3+} is approximately 2:1. Considerable disordering of Ce/Lu in the Lu^{3+} positions should be present. Reexamining the Tm–S bond distances in $CeTmS_3$, the average values of Tm(3)S_7 and Tm(4)S_7 are 2.77 and 2.86 Å, respectively. Compared to the Shannon's data [22], in which TmS_7 and CeS_7 are 2.77 and 2.91 Å, Tm(4) site is more likely disordered. For δ-$Ln_{2-x}Lu_xS_3$ (Ln = Ce, Pr, Nd; $x = 0.67$–0.71), the four eight-coordinate positions were assigned as Ln^{3+} and the Tm(1), Tm(2), and Tm(3) sites were assigned as Lu^{3+} at the beginning of the

Table 1
Crystallographic data for δ-$Ln_{2-x}Lu_xS_3$ (Ln = Ce, Pr, Nd; $x = 0.67$–0.71)

Formula	δ-$Ce_{1.30}Lu_{0.70}S_3$	δ-$Pr_{1.29}Lu_{0.71}S_3$	δ-$Nd_{1.33}Lu_{0.67}S_3$
F_w	400.86	402.31	405.13
Color	Black	Dark red	Dark red
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/m$ (No. 11)	$P2_1/m$ (No. 11)	$P2_1/m$ (No. 11)
a (Å)	11.0186(7)	10.9623(10)	10.9553(7)
b (Å)	3.9796(3)	3.9497(4)	3.9419(3)
c (Å)	21.6562(15)	21.5165(19)	21.4920(15)
>	101.6860(10)	101.579(2)	101.5080(10)
V (Å^3)	929.93(11)	912.66(15)	909.47(11)
Z	8	8	8
T (K)	193	193	193
λ (Å)	0.71073	0.71073	0.71073
ρ_{calcd} (g cm^{-3})	5.726	5.856	5.918
μ (cm^{-1})	284.95	300.82	306.04
$R(F)^a$	0.0288	0.0407	0.0300
$R_w(F_o^2)^b$	0.0656	0.0987	0.0762

[a] $R(F) = \sum||F_o| - |F_c|| / \sum|F_o|$ for $F_o^2 > 2\sigma(F_o^2)$.
[b] $R_w(F_o^2) = \left[\sum\left[w(F_o^2 - F_c^2)^2\right] \Big/ \sum wF_o^4\right]^{1/2}$.

Table 2
Atomic coordinates and equivalent isotropic displacement parameters for δ-$Ce_{1.30}Lu_{0.70}S_3$

Atom (site)	x	y	z	U_{eq} (Å^2)[a]
Ce1	0.19847(5)	0.25	0.76193(3)	0.00853(13)
Ce2	0.58871(5)	0.25	0.86078(3)	0.00753(13)
Ce3	0.80925(5)	0.25	0.72906(3)	0.00609(12)
Ce4	0.69987(5)	0.25	0.53486(3)	0.00697(13)
Ce5	0.02154(10)	0.25	0.09339(5)	0.0113(2)
Lu1	0.94671(4)	0.25	0.41832(2)	0.00977(11)
Lu2	0.52820(5)	0.25	0.35266(3)	0.00965(13)
Ce/Lu	0.67261(5)	0.25	0.04880(2)	0.00988(18)
Lu4	0.0588(5)	0.25	0.0804(2)	0.0176(10)
S1	0.4135(2)	0.25	0.03938(12)	0.0088(5)
S2	0.2948(2)	0.25	0.36659(11)	0.0069(5)
S3	0.7532(2)	0.25	0.32707(12)	0.0094(5)
S4	0.8554(2)	0.25	0.96392(12)	0.0107(5)
S5	0.9936(2)	0.25	0.22765(12)	0.0089(5)
S6	0.2529(2)	0.25	0.17836(12)	0.0080(5)
S7	0.6208(2)	0.25	0.16832(12)	0.0080(5)
S8	0.1437(2)	0.25	0.51372(12)	0.0089(5)
S9	0.4433(2)	0.25	0.55520(12)	0.0109(5)
S10	0.5364(2)	0.25	0.72589(12)	0.0083(5)
S11	0.9553(2)	0.25	0.63164(12)	0.0104(5)
S12	0.1680(2)	0.25	0.89765(12)	0.0117(5)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 3
Atomic coordinates and equivalent isotropic displacement parameters for δ-$Pr_{1.29}Lu_{0.71}S_3$

Atom (site)	x	y	z	U_{eq} (Å^2)[a]
Pr1	0.19691(8)	0.25	0.76308(4)	0.0084(2)
Pr2	0.58798(8)	0.25	0.86070(4)	0.0075(2)
Pr3	0.80815(8)	0.25	0.72974(4)	0.00628(19)
Pr4	0.69981(8)	0.25	0.53557(4)	0.00693(19)
Pr5	0.0220(4)	0.25	0.09241(17)	0.0087(4)
Lu1	0.94660(6)	0.25	0.41786(3)	0.00951(17)
Lu2	0.52939(6)	0.25	0.35258(3)	0.01012(18)
Pr/Lu	0.67394(7)	0.25	0.04788(3)	0.0094(3)
Lu4	0.051(2)	0.25	0.0793(9)	0.015(3)
S1	0.4140(4)	0.25	0.03935(19)	0.0092(8)
S2	0.2947(3)	0.25	0.36625(18)	0.0071(7)
S3	0.7549(3)	0.25	0.32577(19)	0.0090(8)
S4	0.8567(4)	0.25	0.96457(19)	0.0113(8)
S5	0.9947(3)	0.25	0.22627(19)	0.0095(8)
S6	0.2531(3)	0.25	0.17760(18)	0.0076(7)
S7	0.6222(4)	0.25	0.16747(19)	0.0090(7)
S8	0.1442(3)	0.25	0.51375(19)	0.0086(7)
S9	0.4424(4)	0.25	0.55476(19)	0.0107(8)
S10	0.5369(4)	0.25	0.72688(18)	0.0092(7)
S11	0.9543(4)	0.25	0.6323(2)	0.0111(8)
S12	0.1657(4)	0.25	0.89822(19)	0.0112(8)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

refinement cycles. Two large residual electron density peaks approximately 0.5 Å away from each other were found in the original place of Tm(4). Each of these sites was assigned as Ln^{3+} positions. The one with longer Ln–S bond distances was named as Ln(5) (Ln = Ce, Pr, or Nd), and the other one was assigned as Lu(4). It has to be

Table 4
Atomic coordinates and equivalent isotropic displacement parameters for δ-$Nd_{1.33}Lu_{0.67}S_3$

Atom (site)	x	y	z	U_{eq} (Å^2)[a]
Nd1	0.19518(5)	0.25	0.76324(3)	0.00894(14)
Nd2	0.58694(5)	0.25	0.85947(3)	0.00822(14)
Nd3	0.80693(5)	0.25	0.72945(3)	0.00681(13)
Nd4	0.70009(5)	0.25	0.53580(3)	0.00763(13)
Nd5	0.0234(3)	0.25	0.09212(12)	0.0082(3)
Lu1	0.94665(4)	0.25	0.41779(2)	0.01036(12)
Lu2	0.53089(4)	0.25	0.35315(2)	0.01107(13)
Nd/Lu	0.67466(5)	0.25	0.04720(2)	0.00911(19)
Lu4	0.049(2)	0.25	0.0816(10)	0.013(3)
S1	0.4146(2)	0.25	0.04108(12)	0.0094(5)
S2	0.2955(2)	0.25	0.36661(12)	0.0069(5)
S3	0.7555(2)	0.25	0.32486(13)	0.0100(5)
S4	0.8566(3)	0.25	0.96404(13)	0.0110(5)
S5	0.9960(2)	0.25	0.22621(13)	0.0094(5)
S6	0.2545(2)	0.25	0.17833(12)	0.0087(5)
S7	0.6232(2)	0.25	0.16816(12)	0.0091(5)
S8	0.1452(2)	0.25	0.51344(12)	0.0091(5)
S9	0.4426(2)	0.25	0.55385(13)	0.0115(5)
S10	0.5367(2)	0.25	0.72630(12)	0.0090(5)
S11	0.9535(3)	0.25	0.63255(13)	0.0106(5)
S12	0.1628(2)	0.25	0.89773(12)	0.0103(5)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

mentioned, switching the Ln(5) and Lu(4) positions as well as disordering of Ln(5)/Lu(4) at one site were both tried, and gave poorer residuals. The refinement of occupancies of Ln(5) and Lu(4) showed 3:2 ratio of Ln^{3+}:Lu^{3+}, which requires more disordering in other Lu^{3+} sites. In the next step, Ln/Lu were both assigned at Lu(3) positions. This lowered the R_1 value and the weighting scheme to an even greater extent. The final refinements gave rise to formulas of δ-$Ce_{1.30}Lu_{0.70}S_3$, δ-$Pr_{1.29}Lu_{0.71}S_3$, and δ-$Nd_{1.33}Lu_{0.67}S_3$, which are consistent with the Ln:Lu ratios from calibrated EDX results. The standard deviation on the composition from the refinements is 0.01.

2.4. Powder X-ray diffraction

Powder X-ray diffraction patterns were collected with a Rigaku Miniflex powder X-ray diffractometer using Cu K ($\lambda = 1.54056$ Å) radiation.

2.5. Magnetic susceptibility measurements

Magnetism data were measured on powders in gelcap sample holders with a Quantum Design MPMS 7 T magnetometer/susceptometer between 2 and 300 K and in applied fields up to 7 T. DC susceptibility measurements were made under zero-field-cooled conditions with an applied field of 0.1 T. Susceptibility values were corrected for the sample diamagnetic contribution according to Pascal's constants [23] as well as for the sample holder diamagnetism. θ_p values were obtained from extrapolations from fits between 100 and 300 K. In addition, ZFC and FC data were collected as follows: the samples were first zero

Table 5
Selected bond distances (Å) for δ-$Ln_{2-x}Lu_xS_3$ (Ln = Ce, Pr, Nd; x = 0.67–0.71)

Formula	δ- $Ce_{1.30}Lu_{0.70}S_3$	δ-$Pr_{1.29}Lu_{0.71}S_3$	δ-$Nd_{1.33}Lu_{0.67}S_3$
Ln(1)–S(3) × 2	2.8940(19)	2.870(3)	2.858(2)
Ln(1)–S(5) × 2	2.9466(19)	2.925(3)	2.918(2)
Ln(1)–S(7) × 2	2.9978(19)	2.980(3)	2.974(2)
Ln(1)–S(10)	3.957(3)	3.957(4)	3.976(3)
Ln(1)–S(11)	3.476(3)	3.462(4)	3.454(3)
Ln(1)–S(12)	3.025(3)	2.995(4)	2.981(3)
Ln(2)–S(1) × 2	2.9421(19)	2.923(3)	2.910(2)
Ln(2)–S(4)	3.312(3)	3.321(4)	3.336(3)
Ln(2)–S(6) × 2	2.8850(18)	2.862(3)	2.8507(19)
Ln(2)–S(7) × 2	3.0162(19)	3.002(3)	2.998(2)
Ln(2)–S(10)	2.861(3)	2.821(4)	2.805(3)
Ln(3)–S(2) × 2	2.9331(18)	2.916(3)	2.9122(19)
Ln(3)–S(5) × 2	2.9551(19)	2.941(3)	2.938(2)
Ln(3)–S(6) × 2	3.0007(19)	2.977(3)	2.966(2)
Ln(3)–S(10)	2.993(3)	2.962(4)	2.948(3)
Ln(3)–S(11)	2.901(3)	2.882(4)	2.872(3)
Ln(4)–S(2) × 2	2.9098(18)	2.884(3)	2.8715(19)
Ln(4)–S(8) × 2	2.9615(19)	2.946(3)	2.932(2)
Ln(4)–S(9) × 2	3.001(2)	2.982(3)	2.973(2)
Ln(4)–S(9)	2.948(3)	2.933(4)	2.923(3)
Ln(4)–S(11)	3.150(3)	3.128(4)	3.119(3)
Ln(5)–S(4) × 2	2.832(2)	2.798(5)	2.776(3)
Ln(5)–S(4)	3.022(3)	2.975(5)	2.985(4)
Ln(5)–S(5)	2.985(3)	2.955(6)	2.957(4)
Ln(5)–S(6)	2.825(3)	2.813(4)	2.823(4)
Ln(5)–S(12) × 2	2.920(2)	2.888(4)	2.876(3)
Lu(1)–S(3)	2.597(3)	2.583(4)	2.590(3)
Lu(1)–S(8) × 2	2.7771(18)	2.765(3)	2.7702(19)
Lu(1)–S(8)	2.677(3)	2.675(4)	2.678(3)
Lu(1)–S(11) × 2	2.6020(17)	2.592(3)	2.5933(17)
Lu(2)–S(2)	2.649(2)	2.647(4)	2.652(3)
Lu(2)–S(3)	2.647(3)	2.649(4)	2.649(3)
Lu(2)–S(9) × 2	2.7904(19)	2.779(3)	2.7808(19)
Lu(2)–S(10) × 2	2.6210(16)	2.618(3)	2.6160(17)
Ln/Lu–S(1) × 2	2.7880(18)	2.762(3)	2.7749(19)
Ln/Lu–S(1)	2.820(3)	2.819(4)	2.826(3)
Ln/Lu–S(4)	2.989(3)	2.944(4)	2.930(3)
Ln/Lu–S(7)	2.761(3)	2.744(4)	2.768(3)
Ln/Lu–S(12) × 2	2.7500(18)	2.742(3)	2.7595(19)
Lu(4)–S(4) × 2	2.478(3)	2.487(16)	2.513(16)
Lu(4)–S(4)	3.016(6)	2.921(15)	2.951(18)
Lu(4)–S(5)	3.408(5)	3.34(2)	3.27(2)
Lu(4)–S(6)	2.690(6)	2.736(15)	2.741(18)
Lu(4)–S(12) × 2	3.304(4)	3.20(2)	3.145(19)

field cooled from room temperature and the susceptibility was measured at 100 Oe to 300 K. Then the sample was field cooled at 100 Oe to 2 K and the same measurement was done by increasing with increasing temperatures. There are no differences between ZFC and FC data at the measured temperatures.

2.6. UV-vis-NIR diffuse reflectance spectroscopy

The diffuse reflectance spectra for δ-$Ln_{2-x}Lu_xS_3$ (Ln = Ce, Pr, Nd; x = 0.67–0.71) were measured from 200 to 1500 nm using a Shimadzu UV3100 spectrophotometer equipped with an integrating sphere attachment. The Kubelka–Munk function was used to convert diffuse reflectance data to absorption spectra [24].

3. Results and discussion

3.1. Structures of δ-$Ln_{2-x}Lu_xS_3$ (Ln = Ce, Pr, Nd; x = 0.67–0.71)

The δ-$Ln_{2-x}Lu_xS_3$ (Ln = Ce, Pr, Nd; x = 0.67–0.71) series are isotypic with $CeTmS_3$ [10], which crystallizes in $P2_1/m$ space group with a very complex three-dimensional structure. A view of the unit cell is illustrated in Fig. 1. There are nine crystallographically unique lanthanide sites and 12 sulfide positions. Ln(1) are coordinated to nine S atoms in a tricapped trigonal prismatic environment with two long capping Ln···S contacts. For instance, in δ-$Ce_{1.30}Lu_{0.70}S_3$ the short Ce–S bond distances range from 2.8940(19) to 3.025(3) Å, while the longer contacts are 3.476(3) and 3.957(3) Å. The longest of these can probably be disregarded. Ln(2), Ln(3), and Ln(4) have similar coordination geometries. All of them bond to eight S atoms and occur as bicapped trigonal prisms. Ln(5) and Ln/Lu sites are seven-coordinate in a monocapped trigonal prismatic arrangement. It is worth noting that Ln/LuS_7 has intermediate bond distances. For example, the average value of Ce/LuS_7 is 2.81 Å, which is between 2.91 Å for CeS_7 and 2.75 Å for LuS_7 according to the radii reported by Shannon [22]. Compared to larger lanthanides, Lu^{3+} ions have fewer S neighbors. Both Lu(1) and Lu(2) atoms are bound to six S atoms in octahedral environments. Seven-coordinate Lu(4) atoms are found to have a highly distorted monocapped trigonal prismatic geometry, with two short bonds and three long contacts. In case of δ-$Ce_{1.30}Lu_{0.70}S_3$, Lu(4)–S bond distances are 2.478(3) Å × 2, 2.690(6) Å, 3.016(6) Å, 3.304(4) Å × 2, and 3.408(5) Å. The selected bond distances are listed in Table 5. They are normal compared to the Shannon's data [22].

The complex three-dimensional structure of δ-$Ln_{2-x}Lu_xS_3$ (Ln = Ce, Pr, Nd; x = 0.67–0.71) is constructed from one-dimensional chains of LnS_n (n = 6–9) polyhedra that extend along the b axis. Chains constructed from LnS_9 or LnS_8 polyhedra share opposite trigonal faces with two neighbors along the direction of chain propagation. The small six- and seven-coordinate Ln^{3+} containing units only share edges within the chains. Each LnS_x or LuS_y polyhedra share edges and corners with other in the [ac] plane.

Because there are no S–S bonds in δ-$Ln_{2-x}Lu_xS_3$ (Ln = Ce, Pr, Nd; x = 0.67–0.71), the oxidation states in these compounds can be assigned as +3/+3/−2. This designation is confirmed by both bond–valence sum calculations [26,27] and by magnetic susceptibility measurements (vide infra).

3.2. Magnetic susceptibility

The inverse molar Ln magnetic susceptibilities for δ-$Ln_{2-x}Lu_xS_3$ (Ln = Ce, Pr, Nd; x = 0.67–0.71) in the

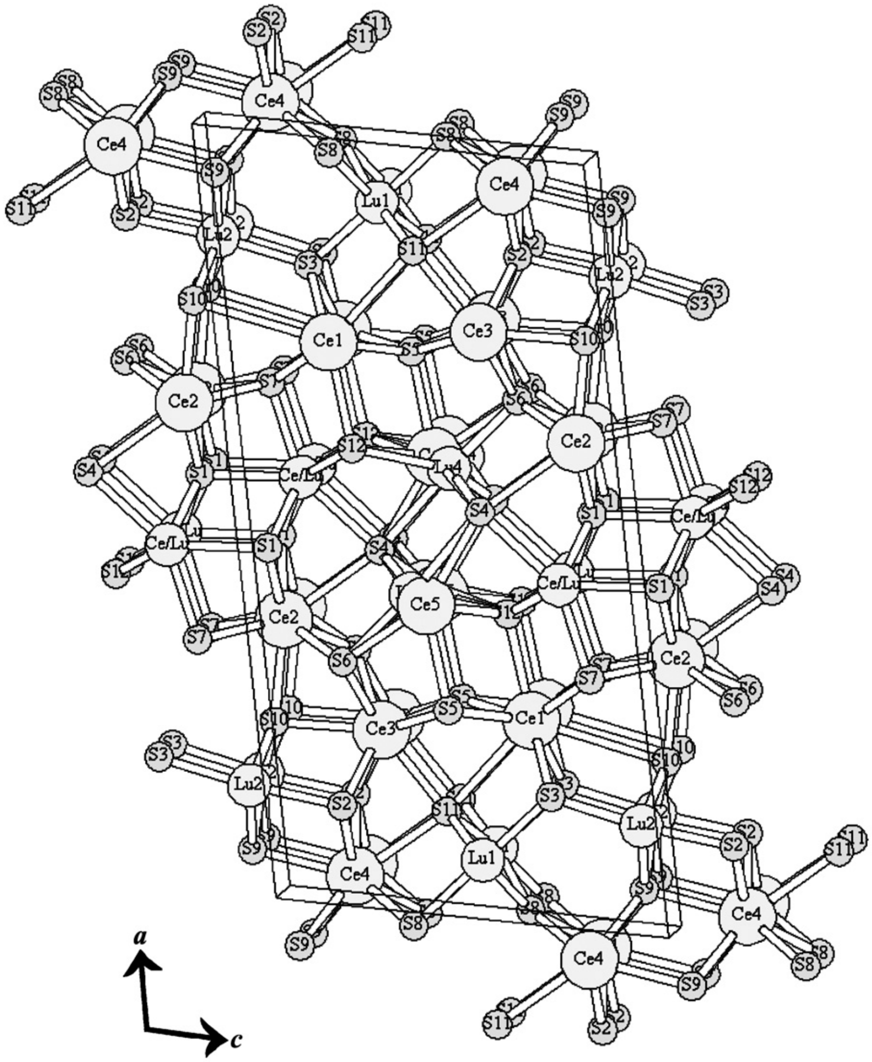

Fig. 1. A view down the *b* axis shows the complex three-dimensional structure of δ-$Ce_{1.30}Lu_{0.70}S_3$.

range of 2–300 K are shown in Figs. 2–4. All three compounds show a deviation from the Curie–Weiss law near 100 K. Magnetic parameters, which are presented in Table 6, were determined from the fits from the Curie–Weiss regions. These compounds do not show evidence of long-range magnetic ordering down to 5 K. δ-$Ce_{1.30}Lu_{0.70}S_3$ has very similar magnetic behavior with β-$LnLn'S_3$ [6] and γ-$LnLn'S_3$ [7] with a large negative value of θ_p of −34(1) K.

The $1/\chi$ data for δ-$Pr_{1.29}Lu_{0.71}S_3$ show a positive, rather than negative, deviation from Curie–Weiss behavior at 120 K. The gradual change in the slope and the negative value of θ_p (−6.0(5) K) may indicate the short-range antiferromagnetic ordering. δ-$Nd_{1.33}Lu_{0.67}S_3$ acts like a intermediate state of δ-$Ce_{1.30}Lu_{0.70}S_3$ and δ-$Pr_{1.29}Lu_{0.71}S_3$. The curvature of the plot starts as upward at 120 K. At lower temperature, it becomes negative. Crystal-field effects and short-range ordering may both contribute to this behavior. The θ_p of δ-$Nd_{1.33}Lu_{0.67}S_3$ is −8(1) K. The experimental effective magnetic moments per Ln ion based

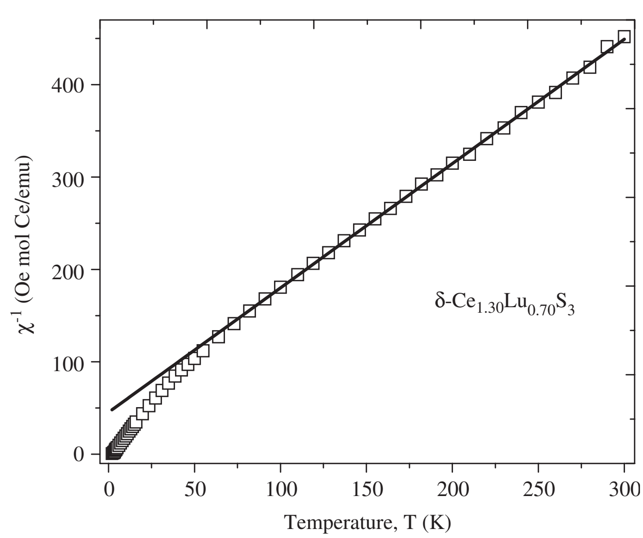

Fig. 2. A plot of inverse molar cerium magnetic susceptibility for δ-$Ce_{1.30}Lu_{0.70}S_3$ between 2 and 300 K. Data were taken under an applied magnetic field of 0.1 T. The straight line represents the fit to Curie–Weiss law in the range of 100–300 K.

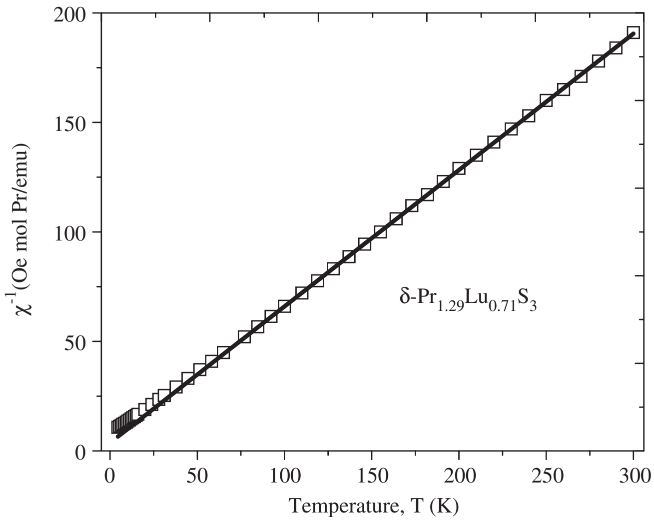

Fig. 3. Temperature dependence of the reciprocal molar praseodymium magnetic susceptibility for δ-$Pr_{1.29}Lu_{0.71}S_3$ under an applied magnetic field of 0.1 T between 2 and 300 K. The straight line represents the fit to Curie–Weiss law in the range of 100–300 K.

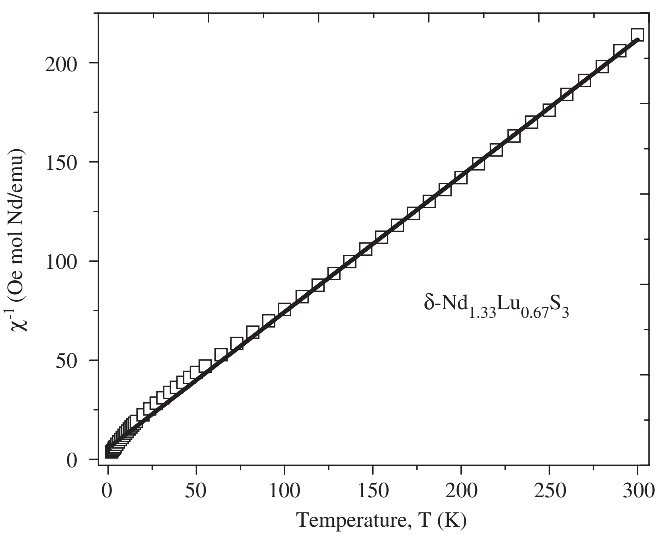

Fig. 4. Inverse molar neodymium magnetic susceptibility vs. T for δ-$Nd_{1.33}Lu_{0.67}S_3$ under an applied magnetic field of 0.1 T between 2 and 300 K. The straight line represents the fit to Curie–Weiss law in the range of 100–300 K.

on the formulas proposed are very close to the theoretical value of the free Ln^{3+} ions as shown in Table 6. As a reference, the experimental moments using the formulas as $LnLuS_3$ (Ln = Ce, Pr, Nd) are 2.82 μ_B for $CeLuS_3$, 4.05 μ_B for $PrLuS_3$, and 3.98 μ_B for $NdLuS_3$, which are larger than the accepted values [25]. This provides further supporting evidence for the disorder refinements.

3.3. Optical properties

The UV–vis–NIR diffuse reflectance spectra are presented in Fig. 5 for δ-$Ln_{2-x}Lu_xS_3$ (Ln = Ce, Pr, Nd; x = 0.67–0.71). The measured band gaps for δ-$Ce_{1.30}Lu_{0.70}S_3$, δ-$Pr_{1.29}Lu_{0.71}S_3$, and δ-$Nd_{1.33}Lu_{0.67}S_3$ are 1.25 eV, 1.38 eV, and 1.50 eV, respectively. They are consistent with the observed colors. δ-$Ce_{1.30}Lu_{0.70}S_3$ is black, while both δ-$Pr_{1.29}Lu_{0.71}S_3$ and δ-$Nd_{1.33}Lu_{0.67}S_3$ are dark red. In addition to the observed band gap for δ-$Nd_{1.33}Lu_{0.67}S_3$, f–f transitions are also apparent in the spectrum of this compound. The band gap results are comparable to the value reported for γ-$LnLn'S_3$ (Ln = La, Ce; Ln′ = Er, Tm, Yb) [7]. δ-$Ce_{1.30}Lu_{0.70}S_3$ has smaller band gap due to the enhanced energy of the $4f^1$ electron. Much like other mixed-lanthanide chalcogenides, the electronic structures of δ-$LnLuS_3$ are tunable based on the choice of lanthanide.

Table 6
Magnetic parameters for δ-$Ln_{2-x}Lu_xS_3$ (Ln = Ce, Pr, Nd; x = 0.67–0.71)

Formula	P_{cal}/μ_B	P_{eff}/μ_B	θ_p/K	R^2
δ-$Ce_{1.30}Lu_{0.70}S_3$	2.54	2.438(5)	−34(1)	0.99952
δ-$Pr_{1.29}Lu_{0.71}S_3$	3.58	3.583(4)	−6.0(5)	0.99989
δ-$Nd_{1.33}Lu_{0.67}S_3$	3.62	3.413(8)	−8(1)	0.99959

[a] P_{cal} and P_{eff} : calculated [25] and experimental effective magnetic moments per Ln ion. [b] Weiss constant (θ_p) and goodness of fit (R^2) obtained from high-temperature (100–300 K) data.

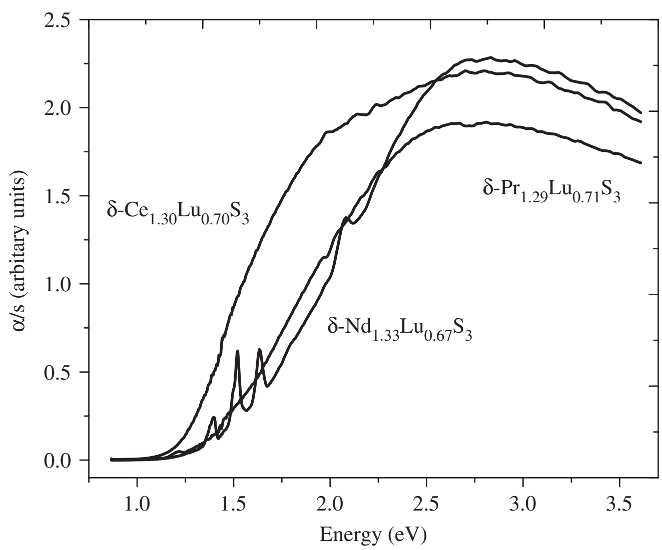

Fig. 5. UV–vis diffuse reflectance spectra of δ-$Ln_{2-x}Lu_xS_3$ (Ln = Ce, Pr, Nd; x = 0.67–0.71).

4. Conclusions

δ-$Ln_{2-x}Lu_xS_3$ (Ln = Ce, Pr, Nd; x = 0.67–0.71) were prepared using an Sb_2S_3 flux and their structures determined by single-crystal X-ray diffraction. These compounds crystallize in the disordered $CeTmS_3$ structure-type. EDX analyses and magnetic measurements support the proposed formulas as δ-$Ce_{1.30}Lu_{0.70}S_3$, δ-$Pr_{1.29}Lu_{0.71}S_3$, and δ-$Nd_{1.33}Lu_{0.67}S_3$. The UV–vis–NIR diffuse reflectance measurements show these compounds to be wide band-gap semiconductors.

5. Supplementary material

Further details of the crystal structure investigation may be obtained from the Fachinformationzentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (Fax: +49-7247-808-666; Email: crysdata@fiz-karlsruhe.de) on quoting depository numbers CSD 417936, 417937, and 417938.

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