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Supporting information for article:

Structure determination of KLaS₂, KPrS₂, KEuS₂, KGdS₂, KL_uS₂, KYS₂, RbYS₂, NaLaS₂ and crystal-chemical analysis of the group 1 and thallium(I) rare-earth sulfide series

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Table S1 Overview of known $M^+Ln^{3+}S_2$ compounds, where M^+ is a group 1 cation as well as Tl^+ ; Ln^{3+} are lanthanides as well as Y^{3+} .

Compound	ICSD	PDF-4	Reference	Space Group	a [Å]	c [Å]	z	Note
LiLaS ₂	-		Ohtani <i>et al.</i> (1987)	$I4\bar{3}d$				Structural type Th_3P_4
LiCeS ₂	-		Ohtani <i>et al.</i> (1987)	$I4\bar{3}d$				Structural type Th_3P_4
LiPrS ₂	44847	04-008-1008	Ballestracci (1965)/ Ballestracci & Bertaut (1965)	$Fm\bar{3}m$	5.686(5)		2	
LiNdS ₂	642202	01-077-2869	Ballestracci (1965)/ Ballestracci & Bertaut (1965)	$Fm\bar{3}m$	5.628(5)		2	
LiNdS ₂	44815	04-005-1435	Ohtani <i>et al.</i> (1987)	$Fm\bar{3}m$	5.635(1)		2	
LiPmS ₂								
LiSmS ₂	642312		Ballestracci (1965)/ Ballestracci & Bertaut (1965)	$Fm\bar{3}m$	5.588		2	
LiSmS ₂	44827		Ohtani <i>et al.</i> (1987)	$Fm\bar{3}m$	5.563(1)		2	
Li _{0.39} Eu _{1.61} S ₂	202421	04-014-0565	Palazzi & Tomas (1987); in Guymont <i>et al.</i> (1990) the corresponding composition is Li _{0.40} Eu _{1.60} S ₂ .	$Fm\bar{3}m$	5.870		2	Electric conductivity of a solid solution; the conductivity is due to the transfer of electrons
LiEuS ₂	44939	04-013-3773	Ballestracci (1965)/ Ballestracci & Bertaut (1965)	$Fm\bar{3}m$	5.606		2	

LiEuS_2	53433	01-071-4393	Palazzi (1986)	$Fm\bar{3}m$	5.572		2	
LiEuS_2		04-005-3039/ 04-005-5275	Palazzi <i>et al.</i> (1987a), Palazzi <i>et al.</i> (1987b)	$Fm\bar{3}m$	5.572		2	In 04-005-3039 of PDF-4 there is referenced the article by Reid <i>et al.</i> (1987). However, there should be referenced the article by Palazzi <i>et al.</i> (1987b).
LiEuS_2	106630		Palazzi & Bretey (1989)	$Fm\bar{3}m$	5.56		2	The value has been assessed from Fig. 1 of the referenced article.
LiEuS_2		04-005-3852 /	Palazzi & Bretey (1989)	$Fm\bar{3}m$	5.55		2	The value has been assessed from Fig. 1 of the referenced article.
LiEuS_2			Guymont <i>et al.</i> (1990)	$Fm\bar{3}m$	5.57		2	Electron diffraction
$\text{Li}_{0.80}\text{Eu}^{2+}_{0.40}\text{Eu}^{3+}_{0.80}\text{S}_2$			Guymont <i>et al.</i> (1990)	$Fm\bar{3}m$	5.65		2	Electron diffraction
$\text{Li}_{0.78}\text{Eu}^{2+}_{0.44}\text{Eu}^{3+}_{0.78}\text{S}_2$		04-005-8523	Guymont <i>et al.</i> (1990)	$Fm\bar{3}m$	5.67		2	Electron diffraction
$\text{Li}_{0.57}\text{Eu}^{2+}_{0.86}\text{Eu}^{3+}_{0.57}\text{S}_2$			Guymont <i>et al.</i> (1990)	$Fm\bar{3}m$	5.73		2	Electron diffraction
$\text{Li}_{0.37}\text{Eu}^{2+}_{1.26}\text{Eu}^{3+}_{0.37}\text{S}_2$			Guymont <i>et al.</i> (1990)	$Fm\bar{3}m$	5.80		2	Electron diffraction
$\text{Li}_{0.20}\text{Eu}^{2+}_{1.60}\text{Eu}^{3+}_{0.20}\text{S}_2$			Guymont <i>et al.</i> (1990)	$Fm\bar{3}m$	5.87		2	Electron diffraction
LiGdS_2	635897		Ballestracci (1965)/	$Fm\bar{3}m$	5.530		2	

			Ballestracci & Bertaut (1965)					
LiGdS ₂	44828	04-005-1434	Ohtani <i>et al.</i> (1987)	<i>Fm</i> $\bar{3}$ <i>m</i>	5.521(1)		2	
LiTbS ₂	642317	01-077-2879	Ballestracci (1965)/ Ballestracci & Bertaut (1965)	<i>Fm</i> $\bar{3}$ <i>m</i>	5.505		2	
LiTbS ₂	642318	04-005-1432	Ohtani <i>et al.</i> (1987)	<i>Fm</i> $\bar{3}$ <i>m</i>	5.489(1)		2	
LiTbS ₂			Plug & Prodan (1978)	<i>Fm</i> $\bar{3}$ <i>m</i>			2	disorder
LiTbS ₂		04-007-9874		<i>R</i> $\bar{3}$ <i>m</i>	3.891	19.066	3	The unit cell parameters are given in PDF-4 but not in the referenced article by Plug & Prodan (1978), z(S)=0.231
LiDyS ₂	44958	04-005-1451	Ohtani <i>et al.</i> (1987)	<i>R</i> $\bar{3}$ <i>m</i>	3.897(1)	18.47(1)	3	In ICSD given z(S)=0.246 but it is not given in the referenced article
LiDyS ₂	44831	04-005-1430	Ohtani <i>et al.</i> (1987)	<i>Fm</i> $\bar{3}$ <i>m</i>	5.468(1)		2	
LiDyS ₂	629899		Ballestracci (1965)/ Ballestracci & Bertaut (1965)	<i>Fm</i> $\bar{3}$ <i>m</i>	5.474		2	
LiHoS ₂			Ballestracci (1965)/ Ballestracci & Bertaut (1965)/ Verheijen <i>et al.</i> (1975)	<i>R</i> $\bar{3}$ <i>m</i>	3.898	18.68	3	The data from Verheijen <i>et al.</i> (1975) taken from Ballestracci & Bertaut (1965). Colloques internationaux du

								C.N.R.S. Orsay 28 sept.- 1.oct. 1965, 41-49.
LiHoS ₂	44959	04-005- 1450	Ohtani <i>et al.</i> (1987)	$R\bar{3}m$	3.892(1)	18.55(1)	3	In ICSD is given $z(S)=0.247$, however, $z(S)$ is missing in the referenced article.
LiHoS ₂	44832	04-005- 1431	Ohtani <i>et al.</i> (1987)	$Fm\bar{3}m$	5.453(1)		2	
LiErS ₂	630736		Ballestracci (1965)/ Ballestracci & Bertaut (1965)	$R\bar{3}m$	3.875	18.63	3	
LiErS ₂	44960	04-005- 1452	Ohtani <i>et al.</i> (1987)	$R\bar{3}m$	3.881(1)	18.65(1)	3	In ICSD is given $z(S)=0.248$, however, $z(S)$ is missing in the referenced article.
LiErS ₂	44833	04-005- 1428	Ohtani <i>et al.</i> (1987)	$Fm\bar{3}m$	5.435(1)		2	
LiTmS ₂	-	04-001- 8395	Tromme (1971)	$R\bar{3}m$	3.829(9)	18.48(9)		
LiYbS ₂			Ballestracci (1965)/ Ballestracci & Bertaut (1965)	$R\bar{3}m$	3.842	18.54	3	
LiLuS ₂	-	04-001- 8387	Tromme (1971)	$R\bar{3}m$	3.813(4)	18.41(2)	3	
LiYS ₂	44830	04-005- 1433	Ohtani <i>et al.</i> (1987)	$Fm\bar{3}m$	5.485(1)		2	

LiYS_2	44957	04-005-1449	Ohtani <i>et al.</i> (1987)	$R\bar{3}m$	3.898(1)	18.56(1)	3	
LiYS_2	642239	01-077-2880/04-002-2230	Ballestracci (1965)/ Ballestracci & Bertaut (1965)/ Hoppe (1965)	$Fm\bar{3}m$	5.473		3	In the referenced article by Hoppe(1965) a= 5.47(3) Å.
LiYS_2			Hoppe (1965)	$Fm\bar{3}m$	5.47(3)		3	
LiYS_2		00-046-1052 / 04-005-3892	Kipp <i>et al.</i> (1990)	$R\bar{3}m$	3.9033(7)	18.522(5)	3	
LiYS_2			Hoppe (1965)					Unknown structure, β - LiYS_2 .
NaLaS_2			This study (1)	$Fm\bar{3}m$	5.8806(2)		2	$\text{Na}_{1.196(105)}\text{Ca}_{0.06(3)}\text{Mn}_{0.012(2)}$ $\text{La}_{0.963(41)}\text{S}_{2.000(35)}$ / 8 points by electron microprobe/20kV
NaLaS_2			This study (2)	$Fm\bar{3}m$	5.8766(9)		2	$\text{Na}_{1.196(105)}\text{Ca}_{0.06(3)}\text{Mn}_{0.012(2)}$ $\text{La}_{0.963(41)}\text{S}_{2.000(35)}$ / 8 points by electron microprobe/20kV
NaLaS_2	43304	01-089-2651	Ballestracci & Bertaut (1964)/ Ballestracci & Bertaut (1965)	$Fm\bar{3}m$	5.881		2	
NaLaS_2	641483	00-038-0848	Sato <i>et al.</i> (1984)	$Fm\bar{3}m$	5.878		2	+ Th_3P_4 type
NaLaS_2		00-038-1391/ 04-007-		$Fm\bar{3}m$	5.87523(13)		2	

		4817						
NaLaS ₂		04-002-2229		<i>Fm</i> $\bar{3}$ <i>m</i>	5.879		2	In the referenced article by Hoppe(1965) <i>a</i> = 5.87(9) Å.
NaLaS ₂			Hoppe (1965)	<i>Fm</i> $\bar{3}$ <i>m</i>	5.87(9)		2	
NaLaS ₂		04-005-1538		<i>Fm</i> $\bar{3}$ <i>m</i>	5.878		2	
NaCeS ₂	43305	01-089-2652	Ballestracci & Bertaut (1964)/ Ballestracci & Bertaut (1965)	<i>Fm</i> $\bar{3}$ <i>m</i>	5.832		2	
NaCeS ₂	79921	01-083-0816	Mauricot <i>et al.</i> (1995).	<i>Fm</i> $\bar{3}$ <i>m</i>	5.8286(2)		2	Neutron powder diffraction; Rietveld analysis
NaCeS ₂	621569	04-005-1541	Sato <i>et al.</i> (1984)	<i>Fm</i> $\bar{3}$ <i>m</i>	5.825		2	+Th ₃ P ₄ type
NaPrS ₂	43306	04-011-6987	Ballestracci & Bertaut (1964)/ Ballestracci & Bertaut (1965)	<i>Fm</i> $\bar{3}$ <i>m</i>	5.777		2	
NaPrS ₂	644940	04-005-1539	Sato <i>et al.</i> (1984)	<i>Fm</i> $\bar{3}$ <i>m</i>	5.798			+Th ₃ P ₄ type
NaNdS ₂	43307	04-011-6988	Ballestracci & Bertaut (1965)	<i>Fm</i> $\bar{3}$ <i>m</i>	5.803		2	
NaNdS ₂	644911	01-077-3013	Sato <i>et al.</i> (1984)	<i>Fm</i> $\bar{3}$ <i>m</i>	5.740		2	Wrong, it should be NaSmS ₂
NaNdS ₂	644912		Sato <i>et al.</i> (1984)	<i>Fm</i> $\bar{3}$ <i>m</i>	5.777		2	
NaNdS ₂			Sato <i>et al.</i> (1984)	<i>R</i> $\bar{3}$ <i>m</i>	4.089	20.024	3	

NaNdS ₂		04-001-8388	Tromme (1971)	$R\bar{3}m$	4.100(4)	19.90(2)	3	In PDF-4 is given z(S)= 0.231, however, z(S) is missing in the referenced article.
NaNdS ₂			Verheijen <i>et al.</i> (1975)/ Ballestracci & Bertaut (1965)		4.100	19.90	3	The data from Verheijen <i>et al.</i> (1975) taken from Ballestracci & Bertaut (1965). Colloques internationaux du C.N.R.S. Orsay 28 sept.-1.oct. 1965, 41-49.
NaNdS ₂		00-040-1081		$Fm\bar{3}m$	5.768		2	In PDF-4 there is referenced the article by Ohtani <i>et al.</i> (1987) but the data are missing in the referenced article.
NaPmS ₂								
NaSmS ₂		04-005-1542	Sato <i>et al.</i> (1984)	$Fm\bar{3}m$	5.740		2	
NaSmS ₂			Ballestracci & Bertaut (1964)/ Ballestracci & Bertaut (1965)	$R\bar{3}m$	4.056	19.87	3	
NaSmS ₂		04-005-1537	Sato <i>et al.</i> (1984)	$R\bar{3}m$	4.057	19.990	3	In PDF-4 is given z(S)= 0.231 but the data are missing the referenced article.

NaEuS ₂			Ballestracci & Bertaut (1964) / Ballestracci & Bertaut (1965)/ Verheijen <i>et al.</i> (1975)	$R\bar{3}m$	4.042	19.92	3	The data from Verheijen <i>et al.</i> (1975) taken from Ballestracci & Bertaut (1965). In ICSD is given the value z(S)=0.258 which is not given in the referenced article by Ballestracci & Bertaut (1964).
NaEuS ₂		631411	Verheijen <i>et al.</i> (1975)	$R\bar{3}m$	4.042	19.92	3	In ICSD is given z(S)=0.258 which it is not given in the referenced article. The data from Verheijen <i>et al.</i> (1975) were taken from Ballestracci & Bertaut (1965).
NaGdS ₂			Ballestracci & Bertaut (1964) / Ballestracci & Bertaut (1965)/ Verheijen <i>et al.</i> (1975)	$R\bar{3}m$	4.009	19.87	3	The data from Verheijen <i>et al.</i> (1975) taken from Ballestracci & Bertaut (1965). Colloques internationaux du C.N.R.S. Orsay 28 sept.-1.oct. 1965, 41-49.

NaGdS ₂	37332	00-037-1146/ 04-005-1530	Sato <i>et al.</i> (1984)	$R\bar{3}m$	4.019	19.958	3	z(S)=0.259; in the original article z(S)=0.241. This value is given in PDF-4 as well as in ICSD.
NaTbS ₂			Ballestracci & Bertaut (1964)/ Ballestracci & Bertaut (1965)	$R\bar{3}m$	3.989	19.87	3	In Ballestracci & Bertaut (1965) there is a misprint: a=4.989 Å
NaTbS ₂		04-005-1536	Sato <i>et al.</i> (1984)	$R\bar{3}m$	3.994	19.919	3	In PDF-4 is given z(S)=0.231 but z(S) is missing in the referenced article.
NaDyS ₂	629966		Ballestracci & Bertaut (1964)/ Ballestracci & Bertaut (1965)/ Verheijen <i>et al.</i> (1975)	$R\bar{3}m$	3.978	19.92	3	The data from Verheijen <i>et al.</i> (1975) taken from Ballestracci & Bertaut (1965). Colloques internationaux du C.N.R.S. Orsay 28 sept.-1.oct. 1965, 41-49. In ICSD is given the value z(S)=0.258 which is not given in the referenced article by Ballestracci & Bertaut (1965).
NaDyS ₂		04-005-1531	Sato <i>et al.</i> (1984)	$R\bar{3}m$	3.979	19.898	3	In PDF-4 is given z(S)=

								0.231 but these data are missing in the referenced article.
NaDyS ₂		04-009-7605	Romero <i>et al.</i> (1998).		3.9746	19.903	3	In PDF-4 is given z(S)=0.231 but z(S) is missing in the referenced article.
NaHoS ₂	56229	01-075-6377 / 03-065-6738	Ballestracci & Bertaut (1964)/ Ballestracci & Bertaut (1965)/ Brüesch & Schüler(1971)/ Verheijen <i>et al.</i> (1975)	$R\bar{3}m$			3	J. of Physics and Chemistry of Solids (1971)/ z(S)=0.240 determined from ionic radii. The data from Verheijen <i>et al.</i> (1975) taken from Ballestracci & Bertaut (1965). Colloques internationaux du C.N.R.S. Orsay 28 sept.-1.oct. 1965, 41-49.
NaHoS ₂		04-005-1535	Sato <i>et al.</i> (1984)	$R\bar{3}m$	3.960	19.885	3	
NaHoS ₂	73480	01-081-2051	Schleid & Lissner (1993)	$R\bar{3}m$			3	Guinier - powder/lattice parameters applied for single cryst. det. given in ICSD; z(S)=0.25749(8)

NaHoS ₂			Schleid & Lissner (1993)	$R\bar{3}m$	3.9556(5)	19.848(4)	3	Single-crystal determination; z(S)=0.25749(8)
NaErS ₂	30250	01-075-0906	Ballestracci & Bertaut (1964)/ [also Ballestracci & Bertaut (1965)/ Verheijen <i>et al.</i> (1975)]	$R\bar{3}m$	3.939	19.98	3	In ICSD z(S)=0.258; this value is given in the referenced article by Ballestracci & Bertaut (1964); it is repeated in the article by Ballestracci & Bertaut (1965).
NaErS ₂	630807		Verheijen <i>et al.</i> (1975)	$R\bar{3}m$	3.939	19.98	3	z(S)=0.258 (Verheijen <i>et al.</i> (1975) – this value has been taken from Ballestracci & Bertaut (1964). The lattice parameters in Verheijen <i>et al.</i> (1975) were taken from Ballestracci & Bertaut (1965).
NaErS ₂	630806	03-065-6068	Brüesch & Schüler (1971)/ [also Ballestracci & Bertaut (1965)/ Verheijen <i>et al.</i> (1975)]	$R\bar{3}m$			3	z(S)= 0.258 determined from the ionic radii, the lattice parameters taken from Ballestracci & Bertaut (1964)
NaErS ₂	73481	04-011-4755	Schleid & Lissner (1993)	$R\bar{3}m$	3.9331(2)	19.8003(9)	3	Guinier - powder/ionic radii applied for single

								cryst. det. in ICSD; in PDF-4 is given the a axis differently (3.9321 Å) to the referenced article; in PDF-4 as well as in ICSD $z(S)=0.25741$
NaErS ₂			Schleid & Lissner (1993)	$R\bar{3}m$	3.9335(6)	19.808(5)	3	Single crystal determination; $z(S)=0.25741(8)$
NaErS ₂	630677	04-005-1532	Sato <i>et al.</i> (1984)	$R\bar{3}m$	3.949	19.874	3	In PDF-4 is given $z(S)=0.231$ but $z(S)$ is missing in the referenced article. In ICSD is given $z(S)=0.241= z(S)= 0.259$ but $z(S)$ is missing in the referenced article.
NaTmS ₂	73482	01-081-2053	Schleid & Lissner (1993)	$R\bar{3}m$	3.9159(2)	19.7674(9)	3	Guinier - powder/lattice parameters applied for single cryst. det. in ICSD; in ICSD $z(S)=0.25731(9)$
NaTmS ₂			Schleid & Lissner (1993)		3.9179(5)	19.772(6)	3	Single crystal det.; $z(S)=0.25731(9)$
NaTmS ₂		04-001-8394	Tromme (1971)	$R\bar{3}m$	3.915(3)	19.88(2)	3	

NaYbS ₂	400013	04-007-4945	Range <i>et al.</i> (1993)	$R\bar{3}m$	3.895(1)	19.831(6)	3	Single crystal determination, z(S)=0.25831(8)
NaYbS ₂	645002	03-065-5514	Brüesch & Schüler (1971)	$R\bar{3}m$	3..91	20.00	3	Ionic radii applied for the structure determination, z(S)=0.26
NaYbS ₂	73483	01-081-2054	Schleid & Lissner (1993)	$R\bar{3}m$	3.9012(2)	19.7360(9)	3	Guinier – powder/lattice parameters applied for single cryst. det. in ICSD; in ICSD c=19.73599(90). In ICSD z(S)=0.25723(9)
NaYbS ₂			Schleid & Lissner (1993)	$R\bar{3}m$	3.8994(6)	19.735(5)	3	Single-crystal det.; z(S)=0.25723(9)
NaYbS ₂		04-005-1534	Sato <i>et al.</i> (1984)	$R\bar{3}m$	3.929	19.833	3	
NaYbS ₂		04-001-8393	Tromme (1971)/Verheijen <i>et al.</i> (1975)	$R\bar{3}m$	3.902(2)	19.91(1)	3	The lattice parameters in Verheijen <i>et al.</i> (1975) taken from Ballestracci & Bertaut (1965). Colloques internationaux du C.N.R.S. Orsay 28 sept.-1.oct. 1965, 41-49.
NaLuS ₂	73484	01-081-2055	Schleid & Lissner (1993)	$R\bar{3}m$	3.8873(2)	19.7058(9)	3	Guinier – powder. ICSD reports z(S)=0.25716(9)

NaLuS ₂			Schleid & Lissner(1993)	$R\bar{3}m$	3.8841(5)	19.703(6)	3	Single-crystal determination/lattice parameters applied for single cryst. det. in ICSD; z(S)=0.25716(9)
		04-001-8392	Tromme (1971)	$R\bar{3}m$	3.885(3)	19.87(2)	3	In PDF-4 there is given z(S)= 0.231 but z(S) is missing in the referenced article.
NaYS ₂	76543	01-089-5281	Ballestracci & Bertaut (1964)/ Ballestracci & Bertaut (1965)/ Brüesch & Schüler (1971)	$R\bar{3}m$	3.968	19.89	3	z(S)=0.26 determined from ionic radii [Brüesch & Schüler (1971)]
NaYS ₂			Hoppe (1965)	$R\bar{3}m$	3.90(8)	20.18	3	
NaYS ₂		04-001-8389/ 04-005-3891	Tromme (1971)	$R\bar{3}m$	3.966(5)	19.93(2)	3	
NaYS ₂		00-046-1051	Kipp <i>et al.</i> (1990)	$R\bar{3}m$	3.9635(3)	19.893(2)	3	
NaYS ₂		04-005-5215	Abou Ghaloun <i>et al.</i> (1980)	$R\bar{3}m$	3.980	19.900	3	
KLaS ₂	44942		Ballestracci (1965)	$R\bar{3}m$	4.464	21.89(5)	3	Cell parameters from

								powder diffraction; Wrong-probably misprint; probably 4.264 (see also Ballestracci & Bertaut (1965); in ICSD is given $a=b=4.464 \text{ \AA}$, $c=21.89499 \text{ \AA}$, $z(S)=0.256$; the structure taken from ICSD. The structure is not given in the referenced article.
KLaS ₂			Ballestracci & Bertaut (1965)	$R\bar{3}m$	4.264	21.89(5)		
KLaS ₂		01-089- 4261		$R\bar{3}m$	4.464	21.89499	3	Wrong parameters a and b .
KLaS ₂			This work	$R\bar{3}m$	4.2651(4)	21.929(3)	3	$z(S)=0.23717(11)/$ $K_{0.971(8)}La_{1.020(5)}S_{2.00(1)}$ 3 points by electron microprobe
KCeS ₂	351	00-030- 0922/ 04- 008-8072	Plug & Verschoor (1976)	$R\bar{3}m$	4.228(4)	21.80(1)	3	$z(S)= 0.26346(4)$, single crystal determination; in ICSD the lattice parameter $c=21.80(2) \text{ \AA}$.
KCeS ₂	621439		Ballestracci (1965)/ Ballestracci & Bertaut (1965)	$R\bar{3}m$	4.223	21.80	3	Cell parameters from powder diffraction; the

KSmS ₂	44944	01-089-4263	Ballestracci (1965)/ Ballestracci & Bertaut (1965)	$R\bar{3}m$	4.107	21.76	3	Cell parameters from powder diffraction; in ICSD as well as PDF-4 wrong unit cell parameters (4.107 and 21.75999); z(S)=0.268; the structure is given in ICSD but not in the original article by Ballestracci (1965).
KEuS ₂	631365		Ballestracci (1965)	$R\bar{3}m$	4.093	21.85(5)	3	$z(S)=0.268$, the structure is given in ICSD but not in the original article. "Coordinates estimated by the editor in analogy to isotypic compounds." In ICSD the <i>c</i> -parameter is given as 21.855 Å.
KEuS ₂			Ballestracci & Bertaut (1965)	$R\bar{3}m$	4.093	21.85(5)	3	
KEuS ₂			This study		4.0981(3)	21.8212(15)		Single X-ray determination; z(S)= 0.23536(4)/ $K_{0.935(46)}Eu_{0.955(98)}S_{2.00(6)}$ 3 points by electron

								microprobe/16kV
KGdS ₂	44945	01-089-4264	Ballestracci (1965)	$R\bar{3}m$	4.075	21.89	3	Cell parameters from powder diffraction; z(S)=0.267; the structure is given in ICSD but not in the original article by Ballestracci (1965).
KGdS ₂			Ballestracci & Bertaut (1965)	$R\bar{3}m$	4.075	22.89	3	An evident misprint regarding the axis c; it should be 21.89 Å
KGdS ₂			This study - unpublished	$R\bar{3}m$	4.0619(7)	21.894(4)	3	$z(S)= 0.23499(11)$
KGdS ₂			This study - unpublished	$R\bar{3}m$	4.0761(7)	21.894(3)	3	$z(S)= 0.23508(10)$
KGdS ₂			This study		4.0715(7)	21.901(4)	3	$z(S)= 0.23501(17)/K_{0.9296(36)}Gd_{0.98(3)}S_{2.00(3)}$ 4 points by electron microprobe/20kV
KTbS ₂			Ballestracci (1965)/Ballestracci & Bertaut (1965)	$R\bar{3}m$	4.051	21.87	3	
KDyS ₂	44946	01-089-4265	Ballestracci (1965)/Ballestracci & Bertaut (1965)	$R\bar{3}m$	4.030	21.83	3	Cell parameters from powder diffraction; in ICSD and PDF-4 there are given the unit cell parameters 4.03 and 21.82999 Å; $z(S)=0.269$;

								the structure is given in ICSD but not in the referenced article by Ballestracci (1965).
KHoS ₂	44947	01-089-4266	Ballestracci (1965)	$R\bar{3}m$	4.009(5)	21.80	3	Cell parameters from powder diffraction; in ICSD as well as in PDF-4 wrong unit cell parameters 4.0095 and 21.79999, z(S)=0.27; the structure given in ICSD is not given in the referenced article by Ballestracci (1965).
KHoS ₂			Verheijen <i>et al.</i> (1975)/Ballestracci & Bertaut (1965)	$R\bar{3}m$	4.010	21.80	3	Taken from Ballestracci & Bertaut (1965). Colloques internationaux du C.N.R.S. Orsay 28 sept.-1.oct. 1965, 41-49.
KErS ₂	44948	01-074-5813/ 01-089-4267	Ballestracci (1965)/Ballestracci & Bertaut (1965)	$R\bar{3}m$	3.993	21.77	3	Cell parameters from powder diffraction; in ICSD given wrong unit cell parameters: $c=21.7699 \text{ \AA}$. In ICSD is

								given z(S)=0.2705 but it is not given in the referenced article by Ballestracci (1965).
KErS ₂	108429	01-074-5813/ 01-089-4267	Ballestracci (1965)/ Ballestracci & Bertaut (1965)	$R\bar{3}m$	3.993	21.77	3	Cell parameters from powder diffraction; in ICSD there is given z(S)=0.265 but it is not given in the referenced article by Ballestracci (1965).
KTmS ₂		04-001-8391	Tromme (1971)		3.977(4)	21.84(2)		In PDF-4 is given z(S)=0.231 but this value is not given in the referenced article.
KYbS ₂	44949	01-089-4268	Ballestracci (1965)/ Ballestracci & Bertaut (1965)	$R\bar{3}m$	3.964	21.82	3	Cell parameters from powder diffraction; in ICSD as well as in PDF-4 wrong unit cell parameters 3.964 and 21.81999 Å; in ICSD is given z(S)=0.271 but it is not given in the referenced article by

								Ballestracci (1965).
KLuS ₂			This study	$R\bar{3}m$	3.9490(4)	21.871(3)	3	$z(S)=0.23369(15)/K_{0.992(8)}Lu_{1.096(12)}Gd_{0.03(2)}S_{2.00(3)}$ / 4 points by electron microprobe/20kV
KLuS ₂		04-001-8390	Tromme (1971)	$R\bar{3}m$	3.947(2)	21.79(2)	3	In PDF-4 there is given $z(S)=0.231$ but this value is not given in the referenced article.
KYS ₂			This study	$R-3m$	4.0216(5)	21.884(4)	3	X-ray single-crystal structure determination; $z(S)=0.23444(8)/K_{0.95(9)}Y_{0.78(6)}Lu_{0.016(20)}Cu_{0.04(1)}Zn_{0.029(9)}S_{2.00(5)}$ / 4 points by electron microprobe/20kV
KYS ₂			Ballestracci (1965)	$R-3m$	4.022(5)	21.85(5)	3	
KYS ₂			Ballestracci & Bertaut (1965)	$R-3m$	4.023	21.85(5)	3	
RbLaS ₂	81394	04-011-4782	Bronger <i>et al.</i> (1996)	$R\bar{3}m$	4.296(1)	22.930(6)	3	Lattice parameters determined from a single crystal; $z(S)=0.2337(1)$; In ICSD the lattice parameter

								$c=22.9300(60)$ Å.
RbLaS ₂			Bronger <i>et al.</i> (1973)	$R\bar{3}m$	4.292	22.89	3	Powder, Guinier cam.era
RbLaS ₂	185320		Havlák <i>et al.</i> (2011)				3	In ICSD 185320 is given a=4.280 and c=22.95 Å. (Havlák <i>et al.</i> (2011) make reference to PDF #86-0693, a = 4.30; c = 22.95 Å.)
RbCeS ₂	81395	04-011- 4769	Bronger <i>et al.</i> (1996)	$R\bar{3}m$			3	Lattice parameters determined from a single crystal; $z(S)=0.2334(3)$.
RbCeS ₂	73546	01-073- 9727	Bronger <i>et al.</i> (1993)	$R\bar{3}m$			3	Powder diffraction; single crystal determination : $z(S)=0.2335(2)$.
RbCeS ₂			Bronger <i>et al.</i> (1973)	$R\bar{3}m$	4.246	22.80	3	Powder, Guinier camera
RbPrS ₂	81396	04-011- 4770	Bronger <i>et al.</i> (1996)	$R\bar{3}m$			3	Lattice parameters determined from a single crystal; $z(S)=0.2329(2)$; In ICSD the lattice parameter $c=22.8970(90)$ Å.
			Bronger <i>et al.</i> (1973)	$R\bar{3}m$	4.222	22.87	3	Powder, Guinier camera

RbNdS ₂	81397	04-011-4771	Bronger <i>et al.</i> (1996)	$R\bar{3}m$	4.194(2)	22.894(12)	3	Lattice parameters determined from a single crystal; z(S)=0.2327(1).
RbNdS ₂			Bronger <i>et al.</i> (1973)	$R\bar{3}m$	4.189	22.89	3	Powder, Guinier camera
RbPmS ₂								
RbSmS ₂	81398	04-011-4772	Bronger <i>et al.</i> (1996))	$R\bar{3}m$	4.143(2)	22.880(9)	3	Lattice parameters determined from a single crystal; z(S)=0.2321(1); <i>In ICSD, the lattice parameter c=22.880(9) Å.</i>
RbSmS ₂			Bronger <i>et al.</i> (1973)	$R\bar{3}m$	4.141	22.861	3	Powder, Guinier camera
RbEuS ₂	81399	04-011-4773	Bronger <i>et al.</i> (1996)	$R\bar{3}m$	4.126(2)	22.890(12)	3	Lattice parameters determined from a single crystal; z(S)=0.2319(1).
RbEuS ₂			Bronger <i>et al.</i> (1973)	$R\bar{3}m$	4.119	22.84	3	Powder, Guinier camera
RbGdS ₂	81400	04-011-4774	Bronger <i>et al.</i> (1996)	$R\bar{3}m$	4.110(1)	22.900(7)	3	Lattice parameters determined from a single crystal; z(S)=0.2320(1); <i>In ICSD, the lattice parameter c=22.880(90) Å.</i>

RbGdS ₂			Bronger <i>et al.</i> (1973)	$R\bar{3}m$	4.098	22.88	3	Powder, Guinier camera
RbTbS ₂	81401	04-011-4775	Bronger <i>et al.</i> (1996)	$R\bar{3}m$			3	Lattice parameters determined from a single crystal; z(S)= 0.2315(1) Bronger, W., Eyck, J., Kruse, K., Schmitz, D. Eur. J. Solid State Inorg. Chem. 33, 213,226 (1996); In ICSD, the lattice parameter $c=22.8740(80)$ Å.
RbTbS ₂		00-048-1725		$R\bar{3}m$			3	PDF-4 refers to the article by Bronger <i>et al.</i> (1996) – see above - but there are no such data..
RbTbS ₂			Bronger <i>et al.</i> (1973)	$R\bar{3}m$	4.070	22.80	3	Powder; Guinier camera
RbDyS ₂	81402	04-011-4776	Bronger <i>et al.</i> (1996)	$R\bar{3}m$			3	Lattice parameters determined from a single crystal; z(S)= 0.2312(1).
RbDyS ₂			Bronger <i>et al.</i> (1993)	$R\bar{3}m$	4.052(7)	22.826(5)	3	
RbDyS ₂		00-052-0883		$R\bar{3}m$	4.0531(2)	22.841(2)	3	
RbHoS ₂	81403	04-011-4777	Bronger <i>et al.</i> (1996)	$R\bar{3}m$	4.037(3)	22.844(18)	3	Lattice parameters determined from a

								single crystal; z(S)=0.2309(2).
RbHoS ₂			Bronger <i>et al.</i> (1993)	$R\bar{3}m$	4.023(1)	22.753(7)	3	
RbErS ₂	81404	04-011-4778	Bronger <i>et al.</i> (1996)	$R\bar{3}m$	4.026(3)	22.802(20)	3	Lattice parameters determined from a single crystal; z(S)=0.2311(4).
RbErS ₂			Bronger <i>et al.</i> (1993)	$R\bar{3}m$	4.017(1)	22.774(9)	3	
RbTmS ₂	81405	04-011-4779	Bronger <i>et al.</i> (1996)	$R\bar{3}m$	4.020(1)	22.838(6)	3	Lattice parameters determined from a single crystal; z(S)=0.2305(2).
RbTmS ₂			Bronger <i>et al.</i> (1993)	$R\bar{3}m$	4.006(8)	22.847(7)	3	
RbYbS ₂	81406	04-011-4780	Bronger <i>et al.</i> (1996)	$R\bar{3}m$	3.991(1)	22.717(7)	3	Lattice parameters determined from a single crystal; z(S)=0.2308(1).
RbYbS ₂			Bronger <i>et al.</i> (1993)	$R\bar{3}m$	3.985(1)	22.801(7)	3	
RbLuS ₂	81407	04-011-4781	Bronger <i>et al.</i> (1996)	$R\bar{3}m$	3.991(1)	22.838(7)	3	Lattice parameters determined from a single crystal; z(S)=0.2303(2).
RbLuS ₂			Bronger <i>et al.</i> (1993)	$R\bar{3}m$	3.973(1)	22.818(5)	3	

RbYS ₂			This study	$R\bar{3}m$	4.0444(3)	22.8267(16)	3	Single crystal determination; z(S)= 0.23090(15)/ Rb _{0.875(36)} Y _{0.923(43)} S _{2.000(35)} / 4 points by electron microprobe/16kV.
TlLaS ₂	-		Duczmal & Pawlak (1988); Duczmal & Pawlak (1994)	<i>I</i> 4/ <i>mcm</i>				TlSe type
TlCeS ₂	-		Duczmal & Pawlak (1988); Duczmal & Pawlak (1994)	<i>I</i> 4/ <i>mcm</i>				TlSe type
TlPrS ₂	-		Duczmal & Pawlak (1994)					Grows TlSe (tetragonal, <i>I</i> 4/ <i>mcm</i>) and rhombohedral phase
TlNdS ₂	54291	01-075-6430/ 01-073-7058	Duczmal & Pawlak (1994)	$R\bar{3}m$	4.129	22.22	3	z(S)=0.2683
TlNdS ₂	57403		Duczmal & Pawlak (1994)	$R\bar{3}m$	4.129	22.22	3	z(S)=0.2683
TlPmS ₂	-							
TlSmS ₂	-	04-002-0535	Kabré <i>et al.</i> (1974)		4.13	22.25	3	
TlEuS ₂	631635		Kabré <i>et al.</i> (1974)		4.12	22.34		In Kabré <i>et al.</i> (1987) is written that this structure

								has been partially doped by Eu ²⁺ . In ICSD z(S)=0.264 but it is not given in the referenced article. "Coordinates estimated by editor in analogy to isotopic compounds."
TIEuS ₂	601357	04-004-0518/ 04-041-0897	Kabré <i>et al.</i> (1987)		4.074	22.42	3	The content of Eu ²⁺ is assessed to be 2- 3% on the basis of magnetic measurements. In ICSD z(S)=0.270 but it is not given in the referenced article. "Coordinates estimated by editor in analogy to isotopic compounds."
TIGdS ₂	57323	01-073-8686	Duczmal & Pawlak (1994)		4.048	22.40	3	z(S)=0.2697; in PDF-4 the c-axis is given as 22.4 Å
TIGdS ₂			Kabré <i>et al.</i> (1974)		4.10	22.34	3	
TITbS ₂			Kabré <i>et al.</i> (1974)		4.07	22.37	3	
TIDyS ₂	57244	01-073-8643	Duczmal & Pawlak (1994)		3.998	22.41	3	z(S)=0.2697

TlDyS ₂			Kabré <i>et al.</i> (1974)		4.06	22.35	3	
TlHoS ₂			Kabré <i>et al.</i> (1974)	$R\bar{3}m$	4.04	22.46	3	
TlErS ₂	26315	04-011-6997	Kabré <i>et al.</i> (1974)	$R\bar{3}m$	3.96	22.47	3	<p>ICSD gives wrong reference: see ICSD #631082; z(S)=0.264(1). This value is not given in the referenced article and it was introduced by the editor by "analogy to isotypic compounds"</p>
TlErS ₂			Duczmal & Pawlak (1994)	$R\bar{3}m$	3.961	22.44	3	$z(S)=0.2700$
TlErS ₂	106620	01-072-8809		$R\bar{3}m$	3.961(2)	22.44(1)		<p>In the work by Duczmal & Pawlak (1994) there are no standard uncertainties of the lattice parameters. However, PDF-4 and ICSD make reference to this work. $z(S)=0.2700$</p>
TlErS ₂	631082	03-065-5848	Kabré <i>et al.</i> (1974)	$R\bar{3}m$	4.02	22.47	3	
TlTmS ₂			Kabré <i>et al.</i> (1974)		4.01	22.52	3	
TlYbS ₂	57119	04-011-8515	Duczmal & Pawlak (1994)	$R\bar{3}m$	3.935	22.47	3	$z(S)=0.2704$ given in ICSD
TlYbS ₂			Kabré <i>et al.</i> (1974)		4.01	22.53	3	

TiLuS ₂			Kabré <i>et al.</i> (1974)	$R\bar{3}m$	3.98	22.59	3	
TIYS ₂			Kabré <i>et al.</i> (1974)		4.04	22.47	3	
Modification (I)								
CsLaS ₂	73532	04-013- 8021	Bronger <i>et al.</i> (1993)	$R\bar{3}m$			3	Lattice parameters from powder – Guinier-Simon method; the sample contained traces of other modification (II); single crystal determination: $z(S)=0.2302(4)$
CsLaS ₂			Bronger <i>et al.</i> (1973)	$R\bar{3}m$	4.306	24.08	3	Powder, Guinier camera
CsCeS ₂	73533	04-013- 8022	Bronger <i>et al.</i> (1993)	$R\bar{3}m$			3	Lattice parameters from powder – Guinier-Simon method; the sample contained traces of other modification (II); single crystal determination: $z(S)=0.2298(6)$
					4.262(1)	24.025(5)		

<chem>CsCeS2</chem>			Bronger <i>et al.</i> (1973)	$R\bar{3}m$	4.262	23.99	3	
<chem>CsPrS2</chem>	73534	04-013-8023	Bronger <i>et al.</i> (1993)	$R\bar{3}m$			3	Lattice parameters from powder – Guinier-Simon method; the sample contained traces of other modification (II); single crystal determination: $z(S)=0.2294(2)$
<chem>CsNdS2</chem>	73535	04-013-8024	Bronger <i>et al.</i> (1993)	$R\bar{3}m$			3	Lattice parameters from powder – Guinier-Simon method; the sample contained traces of other modification (II); single crystal determination: $z(S)=0.2294(3)$
<chem>CsPmS2</chem>								
<chem>CsSmS2</chem>	73536	04-013-8025	Bronger <i>et al.</i> (1993)	$R\bar{3}m$			3	Lattice parameters from powder – Guinier-Simon method; the sample contained traces of other modification (II); single crystal
					4.190(2)	23.926(2)		
					4.161(1)	24.072(7)		

								determination: z(S)=0.2285(9)
CsEuS ₂	73537 04-013- 8026		Bronger <i>et al.</i> (1993)	$R\bar{3}m$ 4.137(2)			3	Lattice parameters from powder – Guinier-Simon method; the sample contained traces of other modification (II); single crystal determination: z(S)=0.2281(5)
CsGdS ₂	73538 04-013- 8027		Bronger <i>et al.</i> (1993)	$R\bar{3}m$ 4.116(1)			3	Lattice parameters from powder – Guinier-Simon method; the sample contained traces of other modification (II); single crystal determination: z(S)=0.2287(3)
CsTbS ₂	73539 04-013- 8028		Bronger <i>et al.</i> (1993)	$R\bar{3}m$ 4.102(1)			3	Lattice parameters from powder – Guinier-Simon method; the sample contained traces of other modification (II); single crystal

								determination: z(S)=0.2280(8)
CsDyS ₂	73540 04-013- 8029		Bronger <i>et al.</i> (1993)	$R\bar{3}m$ 4.058(2)			3	Lattice parameters from powder – Guinier-Simon method; the sample contained traces of other modification (II); single crystal determination: z(S)=0.2276(5)
CsHoS ₂	73541 04-013- 8030		Bronger <i>et al.</i> (1993)	$R\bar{3}m$ 4.054(1)			3	Lattice parameters from powder – Guinier-Simon method; the sample contained traces of other modification (II); single crystal determination: z(S)=0.2275(2)
CsErS ₂	73542 04-013- 8031		Bronger <i>et al.</i> (1993)	$R\bar{3}m$ 4.039(1)			3	Lattice parameters from powder – Guinier-Simon method; the sample contained traces of other modification (II); single crystal

								determination: $z(S)=0.2271(3)$
CsTmS ₂	73543 04-013- 8032		Bronger <i>et al.</i> (1993)	$R\bar{3}m$ 4.022(3)			3	Lattice parameters from powder – Guinier-Simon method; the sample contained traces of other modification (II); single crystal determination: $z(S)=0.2270(5)$
CsYbS ₂	73544 04-013- 8033		Bronger <i>et al.</i> (1993)	$R\bar{3}m$ 4.022(3)			3	Lattice parameters from powder – Guinier-Simon method; the sample contained traces of other modification (II); single crystal determination: $z(S)=0.2771(4)$ – probably misprint, probably there should be $z(s)=0.2271(4)$; in ICSD is given the value $z(s)=0.2271(4)$.
CsLuS ₂	73545 04-013- 8034		Bronger <i>et al.</i> (1993)	$R\bar{3}m$ 3..980(2)			3	Lattice parameters from

								powder – Guinier-Simon method; the sample contained traces of other modification (II); single crystal determination: $z(s)=0.2270(7)$
Modification (II)								
CsLaS ₂								
CsCeS ₂								
CsPrS ₂	73548	04-013- 8035	Bronger <i>et al.</i> (1993)	<i>P</i> 6 ₃ /mmc	4.237(3)	16.020(9)	2	$z(S)=0.5963(2)$
CsNdS ₂	602832	01-079- 9425	Bronger <i>et al.</i> (1993)	<i>P</i> 6 ₃ /mmc	4.205(2)	16.043(9)	2	$z(S)=0.595$; this value is not given in the referenced article, and it was introduced by the editor by "analogy to isotopic compounds".
CsPmS ₂								
CsSmS ₂	602833	01-079- 9426	Bronger <i>et al.</i> (1993)	<i>P</i> 6 ₃ /mmc	4.156(3)	16.011(9)	2	$z(S)=0.595$; this value is not given in the referenced article, and it was introduced by the editor by "analogy to

								isotypic compounds".
CsEuS ₂	602834	01-079-9427	Bronger <i>et al.</i> (1993)	<i>P</i> 6 ₃ / <i>mmc</i>	4.131(3)	15.991(7)	2	<i>z(S)=0.595; this value is not given in the referenced article, and it was introduced by the editor by "analogy to isotypic compounds".</i>
CsGdS ₂	602861	01-079-9430	Bronger <i>et al.</i> (1993)	<i>P</i> 6 ₃ / <i>mmc</i>	4.111(2)	16.022(7)	2	<i>z(S)=0.595; this value is not given in the referenced article, and it was introduced by the editor by "analogy to isotypic compounds".</i>
CsTbS ₂	602889	01-079-9436	Bronger <i>et al.</i> (1993)	<i>P</i> 6 ₃ / <i>mmc</i>	4.102(2)	15.989(5)	2	<i>z(S)=0.595; this value is not given in the referenced article, and it was introduced by the editor by "analogy to isotypic compounds".</i>
CsDyS ₂	602845	01-079-9429	Bronger <i>et al.</i> (1993)	<i>P</i> 6 ₃ / <i>mmc</i>	4.059(1)	15.980(9)	2	<i>z(S)=0.595; this value is not given in the referenced article, and it was introduced by the editor by "analogy to</i>

								isotypic compounds".
CsHoS ₂	602874	01-079-9431	Bronger <i>et al.</i> (1993)	<i>P</i> 6 ₃ / <i>mmc</i>			2	<i>z(S)=0.595; this value is not given in the referenced article, and it was introduced by the editor by "analogy to isotypic compounds".</i>
					4.052(2)	15.995(6)		
CsErS ₂	602875	01-079-9432	Bronger <i>et al.</i> (1993)	<i>P</i> 6 ₃ / <i>mmc</i>			2	<i>z(S)=0.595; this value is not given in the referenced article, and it was introduced by the editor by "analogy to isotypic compounds".</i>
					4.041(1)	16.001(4)		
CsTmS ₂	602876	01-079-9433	Bronger <i>et al.</i> (1993)	<i>P</i> 6 ₃ / <i>mmc</i>			2	<i>z(S)=0.595; this value is not given in the referenced article, and it was introduced by the editor by "analogy to isotypic compounds".</i>
					4.020(4)	15.959(1)		
CsYbS ₂	603271	01-079-9508	Bronger <i>et al.</i> (1993)	<i>P</i> 6 ₃ / <i>mmc</i>			2	<i>z(S)=0.595; this value is not given in the referenced article, and it was introduced by the editor by "analogy to</i>
					4.022(2)	15.925(1)		

								isotypic compounds".
CsLuS ₂	602878	01-079-9435	Bronger <i>et al.</i> (1993)	P6 ₃ /mmc			2	<i>z(S)=0.595; this value is not given in the referenced article, and it was introduced by the editor by "analogy to isotypic compounds".</i>
					3.980(8)	15.951(7)		

Table S2 Overview of crystal-chemical considerations in group 1 and Tl(I) rare-earth sulphides.

Dependence of crystal-chemical variables	1	2		5	6		8		10
$a_{\text{Hex}} \sim Z$									
$c_{\text{Hex}} \sim Z$				5	6				10
$V_{\text{cell}} \sim Z$								9	
$\alpha_{\text{Rhomb}} \sim Z$	1								
$c_{\text{Hex}}/a_{\text{Hex}}$	1								10
$r^{3+}_{\text{ion}} \sim Z$					6				
$z(S^{2-}) \sim Z$ (for $\alpha\text{-NaFeO}\sim 2\sim$ type)				5	6				10
$a_{\text{Hex}} \sim r^{3+}_{\text{ion}}$			3	4					
$c_{\text{Hex}} \sim r^{3+}_{\text{ion}}$				4					
$a_{\text{Cub}} \sim r^{3+}_{\text{ion}}$				4					
$a_{\text{cub}} \sim Z$		2							10
$c_{\text{Hex}}/a_{\text{Hex}} \sim r^{3+}_{\text{ion}}/r^+_{\text{ion}}$			3						

$r^{3+}_{\text{ion}} / r^+_{\text{ion}} \sim Z$						7			
Bond valences									10
$T(M^+), T(Ln^{3+})$									10

- 1) Ballestracci & Bertaut (1964) / NaLnS₂
- 2) Ballestracci (1965) / LiLnS₂, KLnS₂
- 3) Verheijen *et al.* (1975) / LiLnS₂, NaLnS₂, KLnS₂
- 4) Ohtani *et al.* (1987) / LiLnS₂, LiLnSe₂, NaLnS₂, NaLnSe₂
- 5) Bronger *et al.* (1993) / CsLnS₂, RbLnS₂, NaSmSe₂, KSmSe₂, NaSmTe₂, KSmTe₂, RbSmTe₂
- 6) Bronger *et al.* (1996) / NaLnS₂, KLnS₂, RbLnS₂, CsLnS₂ (anomaly for Gd compounds)
- 7) Brunel *et al.* (1971) / LiLnS₂, NaLnS₂
- 8) Tromme *et al.* (1971) / LiLuS₂, LiTmS₂, NaTmS₂, NaYbS₂, NaLuS₂, KTmS₂, KLuS₂, NaYS₂, NaNdS₂,
- 9) Bronger *et al.* (1973) / RbLaS₂, RbCeS₂, RbPrS₂, RbNdS₂, RbSmS₂, RbEuS₂, RbGdS₂, RbTbS₂, CsLaS₂, CsCeS₂
- 10) This study, LiLnS₂, NaLnS₂, KLnS₂, RbLnS₂, CsLnS₂, TiLnS₂

Table S3 The dependence of the length of the axis c [Å] on Z in selected group 1 and thallium(I) rare-earth sulfides (α -NaFeO₂ structural type) as well as in the hexagonal structural type ($P6_3/mmc$) of the second modification of CsLnS₂.

	Reference/ ICSD/PDF-4	Li	Reference/ ICSD/PDF-4	Na	Reference/ ICSD/PDF-4	K	Reference/ ICSD/PDF-4	Rb
La					This study	21.929(3)	Bronger <i>et al.</i> (1996)/ ICSD: 81394/ PDF-4: 04-011-4782	22.930(6)
Ce					Plug & Verschoor (1976)/ ICSD: 351/ PDF-4: 00-030- 0922/ 04- 008-8072	21.80(1)	Bronger <i>et al.</i> (1996)/ ICSD: 81395/ PDF-4: 04-011-4679	22.851(22)
Pr					This study	21.8920(14)	Bronger <i>et al.</i> (1996) / ICSD: 81396/ PDF-4: 04- 011-4770	22.8970(90)
Nd			Sato <i>et al.</i> (1984)	20.024	Ballestracci (1965)	21.83	Bronger <i>et al.</i> (1996) / ICSD: 81397/ PDF-4:	22.894(12)

						04-011-4771	
Pm							
Sm			Sato <i>et al.</i> (1984) / PDF-4: 04-005-1537	19.990	Ballestracci (1965)/ ICSD:44944/ PDF4: 01-089-4263	21.76	Bronger <i>et al.</i> (1996)/ ICSD: 81398/ PDF-4: 04-011-4772
Eu			Ballestracci & Bertaut (1964)/ ICSD: 631411	19.92	This study	21.8212(15)	Bronger <i>et al.</i> (1996)/ ICSD: 81399/ PDF-4: 04-011-4773
Gd			Sato <i>et al.</i> (1984) / ICSD: 37332/ PDF-4: 00-037-1146/ 04-005-1530	19.958	This study	21.901(4)	Bronger <i>et al.</i> (1996) / ICSD: 81400/ PDF-4: 04- 011-4774
Tb	PDF-4: 04-007-9874	19.066	Sato <i>et al.</i> (1984)/ PDF-4: 04-005-1536	19.919	Ballestracci (1965)	21.87	Bronger <i>et al.</i> (1996) / ICSD: 81401/ PDF-4: 04-011-4775
Dy	Ohtani <i>et</i> <i>al.</i> (1987)/ ICSD:44958/ PDF-4: 04-005-1451	18.47(1)	Sato <i>et al.</i> (1984)/PDF-4: 04-005-1531	19.898	Ballestracci (1965)/ ICSD:44946/ PDF-4: 01- 089-4265	21.83	Bronger <i>et al.</i> (1996) / ICSD: 81402/ PDF-4: 04-011-4776
Ho	Ohtani <i>et</i>	18.55(1)	Ballestracci & Bertaut (1964)	19.86	Ballestracci (1965)/	21.80	Bronger <i>et al.</i> (1996)/

	<i>al.</i> (1987)/ ICSD: 44959/ PDF-4: 04-005-1450		/ICSD:56229/ PDF-4: 01-075-6377/ 03-065-6738		ICSD:44947/ PDF-4: 01- 089-4266		ICSD: 81403/ PDF-4: 04- 011-4777	
Er	Ohtani <i>et al.</i> (1987)/ ICSD:44960/ PDF-4: 04-005-1452	18.65(1)	Ballestracci & Bertaut (1964)/ ICSD: 30250/ PDF-4: 01-075-0906	19.98	Ballestracci (1965)/ ICSD:44948/ PDF-4: 01- 074-5813/ 01-089-4267	21.77	Bronger <i>et al.</i> (1996)/ ICSD: 81404/ PDF-4: 04-011-4778	22.802(20)
Tm	Tromme (1971)/PDF-4: 04-001-8395	18.48(9)	Schleid & Lissner (1993)/ ICSD: 73482/ PDF-4: 01-081-2053	19.7674(9)	Tromme (1971)/ PDF-4: 04-001-8391	21.84(2)	Bronger <i>et al.</i> (1996)/ ICSD: 81405 /PDF-4: 04-011-4779	22.838(6)
Yb	Ballestracci (1965)	18.540	Schleid & Lissner (1993)/ ICSD: 73483/ PDF-4: 01-081-2054	19.7360(9)	Ballestracci (1965)/ ICSD:44949/ PDF-4: 01- 089-4268	21.82	Bronger <i>et al.</i> (1996) / ICSD: 81406/ PDF-4: 04-011-4780	22.717(7)
Lu	Tromme (1971)/PDF-4: 04-001-8387	18.41(2)	Schleid & Lissner (1993)/ ICSD: 73484/ PDF-4: 01-081- 2055	19.7058(9)	This study	21.871(3)	Bronger <i>et al.</i> (1996) / ICSD: 81407/ PDF-4: 04- 011-4781	22.838(7)
Y	Ohtani <i>et al.</i>	18.56(1)	Ballestracci &	19.89	This study	21.884(4)	This study	22.8267(16)

	(1987)/ ICSD:44957/ PDF-4: 04-005-1449	Bertaut (1964)/Brüesch h & Schüler (1971)/ ICSD: 76543/ PDF-4: 01-089-5281					
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	Reference/ ICSD/PDF-4		Reference/ ICSD/PDF-4		Reference/ ICSD/PDF-4		Reference/ ICSD/PDF-4	
		Cs(I)		Cs(II)		Tl(Duczmal)		Tl(Kabré)
La	Bronger <i>et al.</i> (1993) / ICSD: 73532/ PDF-4: 04-013-8021	24.088(8)						
Ce	Bronger <i>et al.</i> (1993) / ICSD: 73533/ PDF-4: 04-013-8022	24.025(5)						
Pr	Bronger <i>et al.</i> (1993) / ICSD: 73534 / PDF-4: 04-013-8023	24.054(1)	Bronger <i>et al.</i> (1993) / ICSD: 73548 / PDF-4: 04-013-8035	16.020(9)				
Nd	Bronger <i>et al.</i> (1993) / ICSD: 73535 /	23.926(2)	Bronger <i>et al.</i> (1993) / ICSD: 602832	16.043(9)	Duczmal & Pawlak (1994) / ICSD:	22.22		

	PDF-4: 04-013-8024		/ PDF-4: 01-079-9425		54291; ICSD: 57403 / PDF-4: 01-075-6430/ PDF-4: 01-073-7058			
Pm								
Sm	Bronger <i>et al.</i> (1993) / ICSD: 73536 / PDF-4: 04-013-8025	24.072(7)	Bronger <i>et al.</i> (1993) / ICSD: 602833 / PDF-4: 01-079-9426	16.011(9)		Kabré <i>et al.</i> (1974) / PDF-4: 04-002-0535	22.25	
Eu	Bronger <i>et al.</i> (1993) / ICSD: 73537 / PDF-4: 04-013-8026	24.026(8)	Bronger <i>et al.</i> (1993) / ICSD: 602834 / PDF-4: 01-079-9427	15.991(7)		Kabré <i>et al.</i> (1974) / ICSD: 631635	22.34	
Gd	Bronger <i>et al.</i> (1993) / ICSD: 73538 / PDF-4: 04-013-8027	24.043(7)	Bronger <i>et al.</i> (1993) / ICSD: 602861 / PDF-4: 01-079-9430	16.022(7)	Duczmal & Pawlak (1994) / ICSD: 57323/ PDF-4: 01-073-8686	22.40	Kabré <i>et al.</i> (1974)	22.34
Tb	Bronger <i>et al.</i> (1993) / ICSD: 73539 / PDF-4: 04- 013-8028	24.004(4)	Bronger <i>et al.</i> (1993) / ICSD: 602889 / PDF-4: 01-079-9436	15.989(5)		Kabré <i>et al.</i> (1974)	22.37	
Dy	Bronger <i>et al.</i>	24.008(9)	Bronger <i>et al.</i>	15.980(9)	Duczmal &	22.41	Kabré <i>et al.</i>	22.35

	(1993)/ ICSD: 73540 / PDF-4: 04-013-8029		(1993) / ICSD: 602845 / PDF-4: 01-079-9429		Pawlak (1994) / ICSD: 57244/ PDF-4: 01-073-8643		(1974)	
Ho	Bronger <i>et al.</i> (1993) / ICSD: 73541 / PDF-4: 04-013-8030	24.001(9)	Bronger <i>et al.</i> (1993) / ICSD: 602874 / PDF-4: 01-079-9431		15.995(6)		Kabré <i>et al.</i> (1974)	22.46
Er	Bronger <i>et al.</i> (1993) / ICSD: 73542/ PDF-4: 04-013-8031	24.017(5)	Bronger <i>et al.</i> (1993) / ICSD: 602875 / PDF-4: 01-079-9432		16.001(4)	Duczmal & Pawlak (1994) / ICSD:106620/ PDF-4: 01-072-8809	Kabré <i>et al.</i> (1974) / ICSD: 26315	22.47
Tm	Bronger <i>et al.</i> (1993)/ ICSD: 73543 / PDF-4 : 04-013-8032	23.941(5)	Bronger <i>et al.</i> (1993) / ICSD: 602876 / PDF-4: 01-079-9433		15.959(1)		Kabré <i>et al.</i> (1974)	22.52
Yb	Bronger <i>et al.</i> (1993) / ICSD: 73544/ PDF-4: 04-013-8033		Bronger <i>et al.</i> (1993) / ICSD: 603271 / PDF-4: 01-079-9508		15.925(1)	Duczmal & Pawlak (1994) / ICSD: 57119/ PDF-4: 04-011-8515	Kabré <i>et al.</i> (1974)	22.53
Lu	Bronger <i>et al.</i> (1993) / ICSD: 73545/	23.914(8)	Bronger <i>et al.</i> (1993) / ICSD: 602878		15.951(7)		Kabré <i>et al.</i> (1974)	22.59

	PDF-4: 04-013-8034		/ PDF-4: 01-079-9435					
Y						Kabré <i>et al.</i> (1974)	22.47	

Table S4 The dependence of c/a on Z in selected group 1 and thallium(1+) rare-earth sulfides that are isostructural to α -NaFeO₂ as well as in the hexagonal structural type ($P6_3/mmc$) of the second modification of CsLnS₂.

	Reference/ ICSD/PDF-4	Li	Reference/ ICSD/PDF-4	Na	Reference/ ICSD/PDF-4	K	Reference/ ICSD/PDF-4	Rb
La					This study	5.141	Bronger <i>et al.</i> (1996)/ ICSD: 81394/ PDF-4: 04-011-4782	5.3375
Ce					Plug & Verschoor (1976)/ ICSD: 351/ PDF-4: 00-030-0922/ 04-008-8072	5.156	Bronger <i>et al.</i> (1996)/ ICSD: 81395/ PDF-4: 04-011-4679	5.378
Pr					This study	5.222	Bronger <i>et al.</i> (1996) / ICSD: 81396/ PDF-4: 04-011- 4770	5.4245

Nd			Sato <i>et al.</i> (1984)	4.897	Ballestracci (1965)	5.243	Bronger <i>et al.</i> (1996) / ICSD: 81397/ PDF-4: 04-011-4771	5.459
Pm								
Sm			Sato <i>et al.</i> (1984) / PDF-4: 04-005-1537	4.927	Ballestracci (1965)/ ICSD:44944/ PDF4: 01-089-4263	5.298	Bronger <i>et al.</i> (1996)/ ICSD: 81398/ PDF-4: 04-011-4772	5.503
Eu			Ballestracci & Bertaut (1964)/ ICSD: 631411	4.928	Ballestracci (1965)	5.325	Bronger <i>et al.</i> (1996)/ ICSD: 81399/ PDF-4: 04-011-4773	5.548
Gd			Sato <i>et al.</i> (1984) / ICSD: 37332/ PDF-4: 00-037- 1146/ 04-005-1530	4.966	This study	5.379	Bronger <i>et al.</i> (1996) / ICSD: 81400/ PDF-4: 04-011- 4774	5.572
Tb	PDF_4: 04- 007-9874	4.900	Sato <i>et al.</i> (1984)/ PDF- 4: 04-005-1536	4.987	Ballestracci (1965)	5.399	Bronger <i>et al.</i> (1996) / ICSD: 81401/ PDF-4: 04-011-4775	5.606
Dy	Ohtani <i>et</i> <i>al.</i> (1987)/	4.740	Sato <i>et al.</i> (1984)/PDF-4:	5.001	Ballestracci (1965)/	5.417	Bronger <i>et al.</i> (1996) /	5.637

	ICSD:44958/ PDF-4: 04-005-1451		04-005-1531		ICSD:44946/ PDF-4: 01-089- 4265		ICSD: 81402/ PDF-4: 04-011-4776	
Ho	Ohtani <i>et al.</i> (1987)/ ICSD: 44959/ PDF-4: 04-005-1450	4.766	Ballestracci & Bertaut (1964) /ICSD:56229/ PDF-4: 01-075- 6377/ 03-065-6738	5.029	Ballestracci (1965)/ ICSD:44947/ PDF-4: 01-089- 4266	5.437	Bronger <i>et al.</i> (1996)/ ICSD: 81403/ PDF-4: 04-011- 4777	5.659
Er	Ohtani <i>et al.</i> (1987)/ ICSD:44960/ PDF-4: 04-005-1452	4.805	Ballestracci & Bertaut (1964)/ ICSD: 30250/ PDF-4: 01-075-0906	5.072	Ballestracci (1965)/ ICSD:44948/P DF-4: 01-074- 5813/ 01-089-4267	5.452	Bronger <i>et al.</i> (1996)/ ICSD: 81404/ PDF-4: 04-011-4778	5.664
Tm	Tromme (1971)/PDF-4: 04-001-8395	4.826	Schleid & Lissner (1993)/ ICSD: 73482/ PDF-4: 01-081-2053	5.025	Tromme (1971)/ PDF-4: 04-001-8391)	5.492	Bronger <i>et al.</i> (1996)/ ICSD: 81405 /PDF-4: 04-011-4779	5.681
Yb	Ballestracci (1965)	4.826	Schleid & Lissner (1993)/ ICSD: 73483/ PDF-4: 01-081-2054	5.059	Ballestracci (1965)/ ICSD:44949/P DF-4: 01-089- 4268	5.5045	Bronger <i>et al.</i> (1996) / ICSD: 81406/ PDF-4: 04-011-4780	5.692

Lu	Tromme (1971)/PDF-4: 04-001-8387	4.828	Schleid & Lissner (1993)/ ICSD: 73484/ PDF-4: 01- 081-2055	5.069	This study	5.538	Bronger <i>et al.</i> (1996) / ICSD: 81407/ PDF-4: 04-011- 4781	5.722
Y	Ohtani <i>et al.</i> (1987)/ ICSD:44957/ PDF-4: 04-005- 1449)	4.761	Ballestracci & Bertaut (1964)/Brüesc h & Schüler (1971)/ ICSD: 76543/ PDF-4: 01-089-5281	5.013		5.443	This study	5.644

	Reference/ ICSD/PDF-4	Cs(I)	Reference/ ICSD/PDF-4	Cs(II)	Reference/ ICSD/PDF-4	Tl(Duczmal)	Reference/ ICSD/PDF-4	Tl(Kabré)
La	Bronger <i>et al.</i> (1993) / ICSD: 73532/ PDF-4: 04-013-8021	5.598						
Ce	Bronger <i>et al.</i> (1993) / ICSD: 73533/ PDF-4: 04-013-8022	5.637						
Pr	Bronger <i>et al.</i>	5.684	Bronger <i>et al.</i>	3.781				

	(1993) / ICSD: 73534 / PDF-4: 04-013-8023		(1993) / ICSD: 73548 / PDF-4: 04-013-8035					
Nd	Bronger <i>et al.</i> (1993) / ICSD: 73535 / PDF-4: 04-013-8024	5.710	Bronger <i>et al.</i> (1993) / ICSD: 602832 / PDF-4: 01-079-9425	3.815	Duczmal & Pawlak (1994) / ICSD: 54291; ICSD: 57403 / PDF-4: 01-075-6430/ PDF-4: 01-073-7058	5.381		
Pm								
Sm	Bronger <i>et al.</i> (1993) / ICSD: 73536 / PDF-4: 04-013-8025	5.785	Bronger <i>et al.</i> (1993) / ICSD: 602833 / PDF-4: 01-079-9426	3.8525			Kabré <i>et al.</i> (1974) / PDF-4: 04-002-0535	5.387
Eu	Bronger <i>et al.</i> (1993) / ICSD: 73537 / PDF-4: 04-013-8026	5.8076	Bronger <i>et al.</i> (1993) / ICSD: 602834 / PDF-4: 01-079-9427	3.871			Kabré <i>et al.</i> (1974) / ICSD: 631635	5.422
Gd	Bronger <i>et al.</i> (1993) / ICSD: 73538 / PDF-4: 04-013-8027	5.841	Bronger <i>et al.</i> (1993) / ICSD: 602861 / PDF-4: 01-079-9430	3.897	Duczmal & Pawlak (1994) / ICSD: 57323/ PDF-4: 01-073-8686	5.5336	Kabré <i>et al.</i> (1974)	5.449

Tb	Bronger <i>et al.</i> (1993) / ICSD: 73539 / PDF-4: 04- 013-8028	5.852	Bronger <i>et al.</i> (1993) / ICSD: 602889 / PDF-4: 01-079-9436	3.898			Kabré <i>et al.</i> (1974)	5.496
Dy	Bronger <i>et al.</i> (1993)/ ICSD: 73540 / PDF-4: 04-013-8029	5.916	Bronger <i>et al.</i> (1993) / ICSD: 602845 / PDF-4: 01-079-9429	3.937	Duczmal & Pawlak (1994) / ICSD: 57244/ PDF-4: 01-073-8643	5.605	Kabré <i>et al.</i> (1974)	5.505
Ho	Bronger <i>et al.</i> (1993) / ICSD: 73541 / PDF-4: 04-013-8030	5.920	Bronger <i>et al.</i> (1993) / ICSD: 602874 / PDF-4: 01-079-9431	3.947			Kabré <i>et al.</i> (1974)	5.559
Er	Bronger <i>et al.</i> (1993) / ICSD: 73542/ PDF-4: 04-013-8031	5.946	Bronger <i>et al.</i> (1993) / ICSD: 602875 / PDF-4: 01-079-9432	3.960	Duczmal & Pawlak (1994) / ICSD:106620/ PDF-4: 01-072-8809	5.655	Kabré <i>et al.</i> (1974) / ICSD: 26315	5.674
Tm	Bronger <i>et al.</i> (1993)/ ICSD: 73543 / PDF-4 : 04-013-8032	5.9525	Bronger <i>et al.</i> (1993) / ICSD: 602876 / PDF-4: 01-079-9433	3.970			Kabré <i>et al.</i> (1974)	5.616
Yb	Bronger <i>et al.</i> (1993) / ICSD: 73544/	5.946	Bronger <i>et al.</i> (1993) / ICSD: 603271	3.9595	Duczmal & Pawlak (1994) / ICSD:	5.710	Kabré <i>et al.</i> (1974)	5.618

	PDF-4: 04-013-8033		/ PDF-4: 01-079-9508		57119/ PDF-4: 04-011-8515			
Lu	Bronger <i>et al.</i> (1993) / ICSD: 73545/ PDF-4: 04-013-8034	6.0075	Bronger <i>et al.</i> (1993) / ICSD: 602878 / PDF-4: 01-079-9435	4.008		Kabré <i>et al.</i> (1974)	5.676	
Y						Kabré <i>et al.</i> (1974)	5.562	

Table S5 The dependence of the length of the axis a [Å] on Z in selected group 1 and thallium(1+) rare-earth sulfides (α -NaFeO₂ structural type) as well as in the hexagonal structural type ($P6_3/mmc$) of the second modification of CsLnS₂.

	Reference/ ICSD/ PDF-4	Li	Reference/ ICSD/ PDF-4	Na	Reference/ ICSD/ PDF-4	K	Reference/ ICSD/ PDF-4	Rb
La					This study	4.2651(4)	Bronger <i>et al.</i> (1996)/ ICSD: 81394/ PDF-4: 04-011-4782	4.296(1)
Ce					Plug & Verschoor (1976)/ ICSD: 351/	4.228(4)	Bronger <i>et al.</i> (1996)/ ICSD: 81395/ PDF-4:	4.249(3)

				PDF-4: 00-030-0922/ 04-008-8072		04-011-4769	
Pr				This study	4.1925(3)	Bronger <i>et al.</i> (1996) / ICSD: 81396/ PDF-4: 04-011-4770	4.221(2)
Nd		Sato <i>et al.</i> (1984)	4.089	Ballestracci (1965)	4.160(5)	Bronger <i>et al.</i> (1996) /81397 PDF-4: 04-011-4771	4.194(2)
Pm							
Sm		Sato <i>et al.</i> (1984) / PDF-4: 04-005-1537	4.057	Ballestracci (1965)/ Ballestracci & Bertaut (1965)/ ICSD:44944/ PDF-4: 01- 089-4263	4.107	Bronger <i>et al.</i> (1996) / ICSD: 81398/ PDF-4: 04-011-4772	4.143(2)
Eu		Ballestracci & Bertaut (1964) / Ballestracci & Bertaut (1965)/ Verheijen <i>et al.</i> (1975)/ ICSD: 631411	4.042	This study	4.0981(3)	Bronger <i>et al.</i> (1996) / ICSD: 81399/ PDF-4: 04-011-4773	4.126(2)
Gd		Sato <i>et al.</i> (1984) /	4.019	This study	4.0715(7)	Bronger <i>et al.</i>	4.110(1)

			ICSD: 37332 / PDF-4: 00-037-1146/ 04-005-1530				(1996) / ICSD: 81400/ PDF-4: 04-011-4774	
Tb	PDF-4: 04-007-9874	3.891	Sato <i>et al.</i> (1984)/ PDF-4: 04-005-1536	3.994	Ballestracci (1965)/ Ballestracci & Bertaut (1965)	4.051	Bronger <i>et al.</i> (1996) / ICSD: 81401/ PDF-4: 04-011-4775	4.080(1)
Dy	Ohtani <i>et al.</i> (1987)/ ICSD: 44958/ PDF-4: 04-005-1451	3.897(1)	Sato <i>et al.</i> (1984) / PDF-4: 04-005-1531	3.979	Ballestracci (1965)/ Ballestracci & Bertaut (1965)/ ICSD:44946 / PDF-4: 01-089-4265	4.030	Bronger <i>et al.</i> (1996) / ICSD: 81402/ PDF-4: 04-011-4776	4.060(2)
Ho	Ohtani <i>et al.</i> (1987)/ ICSD: 44959/ PDF-4: 04-005-1450	3.892(1)	Ballestracci & Bertaut (1964) / Brüesch & Schüler(1971)/Verheijen <i>et al.</i> (1975)/ ICSD: 56229/ PDF-4: 01-075-6377/ 03-065-6738	3.949	Ballestracci (1965)/44947	4.009(5)	Bronger <i>et al.</i> (1996) / ICSD: 81403/ PDF-4: 04-011-4777	4.037(3)
Er	Ohtani <i>et al.</i> (1987)/ ICSD:	3.881(1)	Ballestracci & Bertaut (1964) / [also Ballestracci &	3.939	Ballestracci (1965)/ Ballestracci &	3.993	Bronger <i>et al.</i> (1996) / ICSD: 81404/	4.026(3)

	44960/ PDF-4: 04-005-1452	Bertaut (1965)/ Verheijen <i>et al.</i> (1975)]/ ICSD: 30250/ 630807/ PDF-4: 01-075-0906	Bertaut (1965)/ ICSD: 44948/ PDF-4: 01-074-5813/ 01-089-4267	PDF-4: 04-011-4778				
Tm	Tromme (1971)/ PDF-4: 04-001-8395	3.829(9)	Schleid & Lissner (1993) / ICSD: 73482/ PDF-4: 01-081-2053	3.9159(2)	Tromme (1971) / PDF-4: 04-001-8391	3.977(4)	Bronger <i>et al.</i> (1996) / ICSD: 81405 / PDF-4: 04-011-4779	4.020(1)
Yb	Ballestracci (1965)	3.842	Schleid & Lissner (1993)/ ICSD: 73483 / PDF-4: 01-081-2054	3.9012(2)	Ballestracci (1965)/ Ballestracci & Bertaut (1965)/ ICSD: 44949/ PDF-4: 01-089-4268	3.96	Bronger <i>et al.</i> (1996) / ICSD: 81406/ PDF-4: 04-011-4780	3.991(1)
Lu	Tromme (1971)/ PDF-4: 04-001-8387	3.813(4)	Schleid & Lissner (1993)/ ICSD: 73484 PDF-4: 01-081-2055	3.8873(2)	This study	3.9490(4)	Bronger <i>et al.</i> (1996) / ICSD: 81407/ PDF-4: 04-011-4781	3.991(1)
Y	Ohtani <i>et al.</i> (1987)/ ICSD: 44957/ PDF-4: 04-005-1449	3.898(1)	Ballestracci & Bertaut (1964)/ Brüesch & Schüler (1971)/ ICSD: 76543/ PDF-4:	3.968	This study	4.0216(5)	This study	4.0444(3)

Sm	Bronger <i>et al.</i> (1993)/ ICSD: 73536/ PDF-4: 04-013-8025	4.161(1)	Bronger <i>et al.</i> (1993)/ ICSD: 602833 / PDF-4: 01-079-9426	4.156(3)		Kabré <i>et al.</i> (1974)	4.13	
Eu	Bronger <i>et al.</i> (1993)/ ICSD: 73537/ PDF-4: 04-013-8026	4.137(2)	Bronger <i>et al.</i> (1993)/ ICSD: 602834 / PDF-4: 01-079-9427	4.131(3)		Kabré <i>et al.</i> (1974)	4.12	
Gd	Bronger <i>et al.</i> (1993)/ ICSD: 73538/ PDF-4: 04-013-8027	4.116(1)	Bronger <i>et al.</i> (1993)/ ICSD: 602861 / PDF-4: 01-079-9430	4.111(2)	Duczmal & Pawlak (1994) / ICSD:57323/ PDF-4: 01-073-8686	4.048	Kabré <i>et al.</i> (1974)	4.10
Tb	Bronger <i>et al.</i> (1993)/ ICSD: 73539/ PDF-4: 04-013-8028	4.102(1)	Bronger <i>et al.</i> (1993)/ ICSD: 602889 / PDF-4: 01-079-9436	4.102(2)		Kabré <i>et al.</i> (1974)	4.07	
Dy	Bronger <i>et al.</i> (1993)/ ICSD:	4.058(2)	Bronger <i>et al.</i> (1993)/	4.059(1)	Duczmal & Pawlak (1994) / ICSD:	3.998	Kabré <i>et al.</i> (1974)	4.06

	73540/ PDF-4: 04-013-8029		ICSD: 602845 / PDF-4: 01-079-9429		57244/ PDF-4: 01-073-8643			
Ho	Bronger <i>et al.</i> (1993)/ ICSD: 73541/ PDF-4: 04-013-8030	4.054(1)	Bronger <i>et al.</i> (1993)/ ICSD: 602874 / PDF-4: 01-079-9431				Kabré <i>et al.</i> (1974)	4.04
Er	Bronger <i>et al.</i> (1993)/ ICSD: 73542/ PDF-4: 04-013-8031	4.039(1)	Bronger <i>et al.</i> (1993)/ ICSD: 602875/ PDF-4: 01-079-9432		Duczmal & Pawlak (1994) / ICSD: 106620/ PDF-4: 01-072-8809	3.961	Kabré <i>et al.</i> (1974) / ICSD: 631082/ PDF-4: 03-065-5848	4.02
Tm	Bronger <i>et al.</i> (1993)/ ICSD: 73543/ PDF-4: 04-013-8032	4.022(3)	Bronger <i>et al.</i> (1993)/ ICSD: 602876/ PDF-4: 01-079-9433				Kabré <i>et al.</i> (1974)	4.01
Yb	Bronger <i>et al.</i> (1993)/ ICSD: 73544/ PDF-4: 04-013-8033	4.022(3)	Bronger <i>et al.</i> (1993)/ ICSD: 603271 PDF-4: 01-079-9508		Duczmal & Pawlak (1994) / ICSD: 57119/ PDF-4: 04-011-8515	3.935	Kabré <i>et al.</i> (1974)	4.01

Lu	Bronger <i>et al.</i> (1993)/ ICSD: 73545/ PDF-4: 04-013-8034	3.980(2)	Bronger <i>et al.</i> (1993)/ ICSD: 602878 PDF-4: 01-079-9435	3.980(8)			Kabré <i>et al.</i> (1974)	3.98
							Kabré <i>et al.</i> (1974)	4.04

Table S6 The fractional $z(S^{2-})$ coordinate in selected group 1 and thallium rare-earth sulfides (α -NaFeO₂ structural type).

	Reference/ ICSD/ PDF-4	$z(S)_{{\text{Li}}^+}$	Reference/ ICSD/ PDF-4	$z(S)_{{\text{Na}}^+}$	Reference/ ICSD/ PDF-4	$z(S)_{{\text{K}}^+}$	Reference/ ICSD/ PDF-4	$z(S)_{{\text{Rb}}^+}$	Reference/ ICSD/ PDF-4	$z(S)_{{\text{Cs}}^+}$	Reference/ ICSD	$z(S)_{{\text{Tl}}^+}$
MLaS ₂					This study	0.23717(11)	Bronger <i>et al.</i> (1996)/ ICSD: 81394/ PDF-4: 04-011-4782	0.2337(1)	Bronger <i>et al.</i> (1993)/ ICSD: 73532/ PDF-4: 04-013- 8021	0.2302(4)		

M ₂ CeS ₂					Plug & Verschoor (1976)/ ICSD: 351/ PDF-4: 00-030-0922/ 04-008-8072	0.23654(4)	Bronger <i>et al.</i> (1996)/ ICSD: 81395/ PDF-4: 04-011-4769	0.2334(3)	Bronger <i>et al.</i> (1993) ICSD: 73533/ PDF-4: 04-013-8022	0.2298(6)	
M ₂ PrS ₂					This study	0.23618(7)	Bronger <i>et al.</i> (1996)/ ICSD: 81396/ PDF-4: 04-011-4770	0.2329(2)	Bronger <i>et al.</i> (1993) ICSD: 73534/ PDF-4: 04-013-8023	0.2294(2)	
M ₂ NdS ₂					Verheijen <i>et al.</i> (1975)/ Lattice parameters taken from Ballestracci (1965)	0.2353(5)	Bronger <i>et al.</i> (1996) / ICSD: 81397/ PDF-4: 04-011-4771	0.2327(1)	Bronger <i>et al.</i> (1993) ICSD: 73535/ PDF-4: 04-013-8024	Duczmal & Pawlak (1994)/ ICSD: 54291/ PDF-4: 01-075-6430/ 01-073-7058	0.2317

MPmS ₂											
MSmS ₂				Ballestracci (1965)/ ICSD: 44944/ PDF-4: 01-089-4263	0.232	Bronger <i>et al.</i> (1996)/ ICSD: 81398 / PDF-4: 04-011-4772	0.2321(1)	Bronger <i>et al.</i> (1993) ICSD: 73536/ PDF-4: 04-013- 8025	0.2285(9)		
MEuS ₂				This study	0.23536(4)	Bronger <i>et al.</i> (1996) ICSD:81399 / PDF-4: 04-011-4773	0.2319(1)	Bronger <i>et al.</i> (1993) ICSD: 73537/ PDF-4: 04-013- 8026	0.2281(5)		
MGdS ₂			Sato <i>et al.</i> (1984) / ICSD: 37332/ PDF-4: 00-037-1146/	0.241	This study	0.23501(17)	Bronger <i>et al.</i> (1996) ICSD: 81400/	0.2320(1)	Bronger <i>et al.</i> (1993) ICSD: 73538/	Duczmal & Pawlak (1994) / ICSD:57323/	0.2303

			04-005-1530				PDF-4: 04-011-4774		PDF-4: 04-013- 8027		PDF-4: 01-073-8686		
MTbS ₂							Bronger <i>et al.</i> (1996) ICSD: 81401/ PDF-4: 04-011-4775	0.2315(1)	Bronger <i>et al.</i> (1993) ICSD: 73539/ PDF-4: 04-013- 8028	0.2280(8)			
MDyS ₂	Ohtani <i>et al.</i> (1987)/ ICSD: 44958/ PDF-4: 04-005- 1451	0.246		Ballestracci (1965)/ ICSD: 44946 /PDF-4: 01-089-4265		Bronger <i>et al.</i> (1996) ICSD: 81402/ PDF-4: 04-011-4776	0.2312(1)	Bronger <i>et al.</i> (1993) ICSD: 73540/ PDF-4: 04-013- 8029	0.2276(5)	Duczmal & Pawlak (1994) / ICSD:57244/ PDF-4: 01-073-8643	0.2303		
MHoS ₂	Ohtani <i>et al.</i> (1987)/ ICSD:	0.247	Ballestracci & Bertaut (1964)/ ICSD:	0.240	Ballestracci (1965)/ ICSD: 44947	0.23	Bronger <i>et al.</i> (1996) ICSD:81403/	0.2309(2)	Bronger <i>et al.</i> (1993) ICSD:	0.2275(2)			

	44959/ PDF-4: 04-005- 1450		56229/ PDF-4: 01-075-6377/ 03-065-6738		/PDF-4: 01-089-4266		PDF-4: 04-011-4777		73541/ PDF-4: 04-013- 8030			
MErS ₂	Ohtani <i>et al.</i> (1987)/ ICSD: 44960/ PDF-4: 04-005- 1452		Ballestracci & Bertaut (1964)/ ICSD: 30250/ PDF-4: 01-075-0906	0.242 0.248	Ballestracci (1965)/ ICSD: 44948 / PDF-4: 01-074-5813/ 01-089-4267		Bronger <i>et al.</i> (1996)/ ICSD:81404/ PDF-4: 04-011-4778	0.2311(4)	Bronger <i>et al.</i> (1993) ICSD: 73542/ PDF-4: 04-013- 8031		Duczmal & Pawlak (1994) / ICSD:106620/ PDF-4: 01-072-8809	0.23
MTmS ₂			Schleid & Lissner (1993)/ ICSD: 73482/ PDF-4: 01-081-2053	0.24269(8)		0.231	Bronger <i>et al.</i> (1996) / ICSD:81405/ PDF-4: 04-011-4779	0.2305(2)	Bronger <i>et al.</i> (1993) ICSD: 73543/ PDF-4: 04-013- 8032	0.2270(7)		
MYbS ₂			Schleid & Lissner (1993)/ ICSD: 73483	0.24277(9)	Ballestracci (1965)/ ICSD:44949/	0.229	Bronger <i>et al.</i> (1996) / ICSD:81406	0.2308(1)	Bronger <i>et al.</i> (1993) ICSD: 0.2271(4)		Duczmal & Pawlak (1994) /	0.2296

			PDF-4: 01-081-2054		PDF-4: 01-089-4268		/ PDF-4: 04-011-4780		73544/ PDF-4: 04-013- 8033		ICSD:57119 / PDF-4: 04-011-8515	
MLuS ₂			Schleid & Lissner (1993)/ ICSD: 73484 PDF-4: 01-081-2055	0.24284(9)	This study		Bronger <i>et al.</i> (1996) / ICSD: 81407 / PDF-4: 04-011-4781	0.2303(2)	Bronger <i>et al.</i> (1993) ICSD: 73545/ PDF-4: 04-013- 8034	0.2270(7)		
MYS ₂					This study	0.23444(8)	This study	0.23090(15)				

Table S7 The thickness T_{M^+} [Å] of the layer M^+S_6 with the monovalent cation M^+ in the α -NaFeO₂ structural type of selected group 1 and thallium rare-earth sulfides.

	Reference/ ICSD/ PDF-4	TLi ⁺	Reference/ ICSD/ PDF-4	TNa ⁺	Reference/ ICSD/ PDF-4	TK ⁺	Reference/ ICSD/ PDF-4	TRb ⁺	Reference/ ICSD/ PDF-4	TCs ⁺	Reference/ ICSD/ PDF-4 Reference/ ICSD/ PDF-4	TTl ⁺
MLaS ₂					This study	4.2175	Bronger <i>et al.</i> (1996)/ ICSD: 81394/ PDF-4: 04-011-4782	4.561	Bronger <i>et al.</i> (1993)/ ICSD: 73532/ PDF-4: 04-013-8021	4.9686		
MCeS ₂					Plug & Verschoor (1976)/ ICSD: 351/ PDF-4:	4.220	Bronger <i>et al.</i> (1996)/ ICSD: 81395/ PDF-4: 04-011-4769	4.5656	Bronger <i>et al.</i> (1993) ICSD: 73533/ PDF-4:	4.975		

					00-030-0922/ 04-008-8072				04-013-8022			
MPrS ₂					This study	4.254	Bronger <i>et al.</i> (1996)/ ICSD: 81396/ PDF-4: 04-011-4770	4.594	Bronger <i>et al.</i> (1993) ICSD: 73534/ PDF-4: 04-013-8023	5.000		
MNdS ₂					Verheijen <i>et al.</i> (1975)/ Lattice parameters taken from Ballestracci (1965)	4.276	Bronger <i>et al.</i> (1996) / ICSD: 81397/ PDF-4: 04-011-4771	4.607	Bronger <i>et al.</i> (1993) ICSD: 73535/ PDF-4: 04-013-8024	4.973	Duczmal & Pawlak (1994)/ ICSD:54291/ PDF-4: 01-075-6430/ 01-073-7058	4.517
MPmS ₂												
MSmS ₂					Ballestracci (1965)/ ICSD: 44944/	4.410	Bronger <i>et al.</i> (1996)/ ICSD: 81398 /	4.628	Bronger <i>et al.</i> (1993) ICSD:	5.047		

					PDF-4: 01-089-4263		PDF-4: 04-011-4772		73536/ PDF-4: 04-013-8025			
MEuS ₂					This study	4.276	Bronger <i>et al.</i> (1996) ICSD:81399 / PDF-4: 04-011-4773	4.633	Bronger <i>et al.</i> (1993) ICSD: 73537/ PDF-4: 04-013-8026	5.057		
MGdS ₂			Sato <i>et al.</i> (1984) / ICSD: 37332/ PDF-4: 00-037-1146/ 04-005-1530	3.6856	This study	4.307	Bronger <i>et al.</i> (1996) ICSD: 81400/ PDF-4: 04-011-4774	4.637	Bronger <i>et al.</i> (1993) ICSD: 73538/ PDF-4: 04-013-8027	5.031	Duczmal & Pawlak (1994) / ICSD:57323/ PDF-4: 01-073-8686	4.616
MTbS ₂							Bronger <i>et al.</i> (1996) ICSD: 81401/ PDF-4:	4.644	Bronger <i>et al.</i> (1993) ICSD: 73539/	5.057		

						04-011-4775		PDF-4: 04-013-8028			
MDyS ₂	Ohtani <i>et al.</i> (1987)/ ICSD: 44958/ PDF-4: 04-005-1451	3.226		Ballestracci (1965)/ ICSD: 44946 /PDF-4: 01-089-4265	4.468	Bronger <i>et al.</i> (1996) ICSD: 81402/ PDF-4: 04-011-4776	4.6626	Bronger <i>et al.</i> (1993) ICSD: 73540/ PDF-4: 04-013-8029	5.077	Duczmal & Pawlak (1994) / ICSD:57244/ PDF-4: 01-073-8643	4.618
MHoS ₂	Ohtani <i>et al.</i> (1987)/ ICSD: 44959/ PDF-4: 04-005-1450	3.202967	Ballestracci & Bertaut (1964)/ ICSD: 56229/ PDF-4: 01-075-6377/ 03-065-6738	3.7072	Ballestracci (1965)/ ICSD: 44947 /PDF-4: 01-089-4266	4.505	Bronger <i>et al.</i> (1996) ICSD:81403/ PDF-4: 04-011-4777	4.661	Bronger <i>et al.</i> (1993) ICSD: 73541/ PDF-4: 04-013-8030	5.080	
MErS ₂	Ohtani <i>et al.</i> (1987)/ ICSD: 44960/ PDF-4: 01-075-0906	3.182933	Ballestracci & Bertaut (1964)/ ICSD: 30250/ PDF-4: 01-075-0906	3.6497	Ballestracci (1965)/ ICSD: 44948 /	4.521	Bronger <i>et al.</i> (1996)/ ICSD:81404/ PDF-4:	4.6565	Bronger <i>et al.</i> (1993) ICSD: 73542/	5.103	Duczmal & Pawlak (1994) / ICSD:106620/

	04-005-1452				PDF-4: 01-074-5813/ 01-089-4267		04-011-4778		PDF-4: 04-013-8031		PDF-4: 01-072-8809	
MTmS ₂			Schleid & Lissner (1993)/ ICSD: 73482/ PDF-4: 01-081-2053	3.5836			Bronger <i>et al.</i> (1996) / ICSD:81405/ PDF-4: 04-011-4779	4.699	Bronger <i>et al.</i> (1993) ICSD: 73543/ PDF-4: 04-013-8032	5.091		
MYbS ₂			Schleid & Lissner (1993)/ ICSD: 73483 PDF-4: 01-081-2054	3.684	Ballestracci (1965)/ ICSD:44949/ PDF-4: 01-089-4268	4.553	Bronger <i>et al.</i> (1996) / ICSD:81406 / PDF-4: 04-011-4780	4.676	Bronger <i>et al.</i> (1993) ICSD: 73544/ PDF-4: 04-013-8033	5.081	Duczmal & Pawlak (1994) / ICSD:57119 / PDF-4: 04-011-8515	4.662
MLuS ₂			Schleid & Lissner (1993)/ ICSD: 73484 PDF-4: 01-081-2055	3.5665	This study	4.359	Bronger <i>et al.</i> (1996) / ICSD: 81407 / PDF-4: 04-011-4781	4.702	Bronger <i>et al.</i> (1993) ICSD: 73545/ PDF-4:	5.085		

								04-013-8034			
MYS ₂				This study	4.328	This study	4.676				

Table S8 The thickness $T_{\text{Ln}^{3+}} \text{[Å]}$ of the layer Ln^{3+}S_6 and Y^{3+}S_6 with the trivalent cation $T_{\text{Ln}^{3+}}/T_{\text{Y}^{3+}}$ in the $\alpha\text{-NaFeO}_2$ structural type of selected group 1 and thallium rare-earth sulfides.

	Reference/ ICSD/ PDF-4	$\text{TLi}^+ \text{[Å]}$	Reference/ ICSD/ PDF-4	$\text{TNa}^+ \text{[Å]}$	Reference/ ICSD/ PDF-4	$\text{TK}^+ \text{[Å]}$	Reference/ ICSD/ PDF-4	$\text{TRb}^+ \text{[Å]}$	Reference/ ICSD/ PDF-4	$\text{TCs}^+ \text{[Å]}$	Reference/ ICSD/ PDF-4	$\text{TTl}^+ \text{[Å]}$
MLaS ₂					This study	3.092	Bronger <i>et al.</i> (1996)/ ICSD: 81394/ PDF-4: 04-011-4782	3.069	Bronger <i>et al.</i> (1993)/ ICSD: 73532/ PDF-4: 04-013-8021	3.061		
M CeS ₂					Plug & Verschoor (1976)/ ICSD: 351/ PDF-4:	3.046	Bronger <i>et al.</i> (1996)/ ICSD: 81395/ PDF-4:	3.049	Bronger <i>et al.</i> (1993) ICSD: 73533/ PDF-4:	3.0336		

					00-030-0922/ 04-008-8072		04-011-4769		04-013-8022			
MPrS ₂					This study	3.0435	Bronger <i>et al.</i> (1996)/ ICSD: 81396/ PDF-4: 04-011-4770	3.0295	Bronger <i>et al.</i> (1993) ICSD: 73534/ PDF-4: 04-013-8023	3.018		
MNdS ₂					Verheijen <i>et al.</i> (1975)/ Lattice parameters taken from Ballestracci (1965)	2.994	Bronger <i>et al.</i> (1996) / ICSD: 81397/ PDF-4: 04-011-4771	3.023	Bronger <i>et al.</i> (1993) ICSD: 73535/ PDF-4: 04-013-8024	3.002	Duczmal & Pawlak (1994)/ ICSD:54291/ PDF-4: 01-075-6430/ 01-073-7058	2.890
MPmS ₂												
MSmS ₂					Ballestracci (1965)/ ICSD: 44944/ PDF-4:	2.843	Bronger <i>et al.</i> (1996)/ ICSD: 81398	2.992	Bronger <i>et al.</i> (1993) ICSD:	2.977		

					01-089-4263		/		73536/			
						PDF-4: 04-011-4772			PDF-4: 04-013-8025			
MEuS ₂				This study	2.998	Bronger <i>et al.</i> (1996) ICSD:81399 /	2.980	Bronger <i>et al.</i> (1993) ICSD: 73537/ PDF-4: 04-011-4773				
MGdS ₂			Sato <i>et al.</i> (1984) / ICSD: 37332/ PDF-4: 00-037-1146/ 04-005-1530	2.967	This study	2.994	Bronger <i>et al.</i> (1996) ICSD: 81400/ PDF-4: 04-011-4774	2.990	Bronger <i>et al.</i> (1993) ICSD: 73538/ PDF-4: 04-013-8027		Duczmal & Pawlak (1994) / ICSD:57323/ PDF-4: 01-073-8686	2.851
MTbS ₂						Bronger <i>et al.</i> (1996) ICSD: 81401/	2.956	Bronger <i>et al.</i> (1993) ICSD: 73539/				
									2.944			

							PDF-4: 04-011-4775		PDF-4: 04-013-8028			
MDyS ₂	Ohtani <i>et al.</i> (1987)/ ICSD: 44958/ PDF-4: 04-005-1451	2.931		Ballestracci (1965)/ ICSD: 44946 /PDF-4: 01-089-4265		Bronger <i>et al.</i> (1996) ICSD: 81402/ PDF-4: 04-011-4776	2.946	Bronger <i>et al.</i> (1993) ICSD: 73540/ PDF-4: 04-013-8029		Duczmal & Pawlak (1994) / ICSD:57244/ PDF-4: 01-073-8643	2.852	
MHoS ₂	Ohtani <i>et al.</i> (1987)/ ICSD: 44959/ PDF-4: 04-005-1450	2.980	Ballestracci & Bertaut (1964)/ ICSD: 56229/ PDF-4: 01-075-6377/ 03-065-6738	2.913	Ballestracci (1965)/ ICSD: 44947 /PDF-4: 01-089-4266		Bronger <i>et al.</i> (1996) ICSD:81403/ PDF-4: 04-011-4777	2.923	Bronger <i>et al.</i> (1993) ICSD: 73541/ PDF-4: 04-013-8030		2.920	
MErS ₂	Ohtani <i>et al.</i> (1987)/ ICSD: 44960/ PDF-4:	3.034	Ballestracci & Bertaut (1964)/ ICSD: 30250/ PDF-4: 01-075-0906	3.010	Ballestracci (1965)/ ICSD: 44948 / PDF-4: 01-074-5813/	2.736	Bronger <i>et al.</i> (1996) ICSD:81404/ PDF-4: 04-011-4778	2.935	Bronger <i>et al.</i> (1993) ICSD: 73542/ PDF-4: 04-013-8030	Duczmal & Pawlak (1994) / ICSD:106620/ PDF-4: 01-073-8643	2.837	

	04-005-1452				01-089-4267				04-013-8031		01-072-8809	
MTmS ₂			Schleid & Lissner (1993)/ ICSD: 73482/ PDF-4: 01-081-2053	3.0056			Bronger <i>et al.</i> (1996) / ICSD:81405/ PDF-4: 04-011-4779	2.917	Bronger <i>et al.</i> (1993) ICSD: 73543/ PDF-4: 04-013-8032	2.889		
MYbS ₂			Schleid & Lissner (1993)/ ICSD: 73483 PDF-4: 01-081-2054	2.895	Ballestracci (1965)/ ICSD:44949/ PDF-4: 01-089-4268		Bronger <i>et al.</i> (1996) / ICSD:81406 / PDF-4: 04-011-4780	2.925	Bronger <i>et al.</i> (1993) ICSD: 73544/ PDF-4: 04-013-8033	2.890	Duczmal & Pawlak (1994) / ICSD:57119 / PDF-4: 04-011-8515	2.828
MLuS ₂			Schleid & Lissner (1993)/ ICSD: 73484 PDF-4: 01-081-2055	3.002	This study		Bronger <i>et al.</i> (1996) / ICSD: 81407 / PDF-4: 04-011-4781	2.904	Bronger <i>et al.</i> (1993) ICSD: 73545/ PDF-4: 04-013-8034	2.885		

MY ₂ S					This study	2.966	This study	2.933				
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Table S9 M⁺-S²⁻ distances [Å] in selected group 1 and thallium rare-earth sulfides.

	Reference/ ICSD/ PDF-4	Li ⁺ -S ²⁻ (cubic) [Å]	Reference/ ICSD/ PDF-4	Li ⁺ -S ²⁻ (rhombohedral) [Å]	Reference/ ICSD/ PDF-4	Na ⁺ -S ²⁻ (cubic) [Å]	Reference/ ICSD/ PDF-4	Na ⁺ -S ²⁻ (rhombohedral) [Å]	Reference/ ICSD/ PDF-4	K ⁺ -S ²⁻ (rhombohedral) [Å]	Reference/ ICSD/ PDF-4	Rb ⁺ -S ²⁻ (rhombohedral) [Å]
MLaS ₂					This study	2.9403			This study		Bronger <i>et al.</i> (1996)/ ICSD: 81394/ PDF-4: 04-011-4782	3.372(2)
MCeS ₂					Sato <i>et al.</i> (1984)/ ICSD: 621569/ PDF-4: 04-005-1541	2.9125			Plug & Verschoor (1976)/ ICSD: 351/ PDF-4: 00-030-0922/ 04-008-8072	3.227	Bronger <i>et al.</i> (1996)/ ICSD: 81395 / PDF-4: 04-011-4769	3.352(7)
MPrS ₂	Ballestracci (1965)/ Ballestracci &	2.843			Sato <i>et al.</i> (1984)/ ICSD: 644940	2.899			This study	3.222(1)	Bronger <i>et al.</i> (1996) /	3.351(4)

	Bertaut (1965)/ ICSD: 44847/ PDF-4: 04-008-1008									ICSD: 81396 / PDF-4: 04-011-4770	
MNdS ₂	Ballestracci (1965)/ Ballestracci & Bertaut (1965)/ ICSD: 642202/ PDF-4: 01-077-2869	2.814			Sato <i>et al.</i> (1984) / ICSD: 644912	2.8885			Verheijen <i>et al.</i> (1975)	Bronger <i>et al.</i> (1996) / ICSD: 81397 / PDF-4: 04-011-4771	3.342(3)
MPmS ₂											3.216
MSmS ₂	Ballestracci (1965)/ Ballestracci & Bertaut (1965)/ ICSD: 642312	2.794			Sato <i>et al.</i> (1984)/ PDF-4: 04-005-1542	2.87			Ballestracci (1965)/ Ballestracci & Bertaut (1965)/ ICSD: 44944/ PDF-4: 01-089-4263	Bronger <i>et al.</i> (1996) / ICSD: 81398 / PDF-4: 04-011-4772	3.330(3)
MEuS ₂	Ballestracci (1965)/ Ballestracci & Bertaut	2.803							This study	Bronger <i>et al.</i> (1996) / ICSD: 81399	3.326(3)
									3.1889(8)		

	(1965)/ ICSD: 44939 / PDF-4: 04-013-3773								/ PDF-4: 04-011-4773	
MGdS ₂	Ballestracci (1965)/ Ballestracci & Bertaut (1965) ICSD: 635897	2.765				Sato et al. (1984)/ ICSD:37332 / PDF:4 00-037-1146/ 04-005-1530	2.9631	This study 3.188(3)	Bronger et al. (1996) / ICSD: 81400 / PDF-4: 04-011-4774	3.326(3)
MTbS ₂	Ballestracci (1965)/ Ballestracci & Bertaut (1965)/ ICSD: 642317 / PDF-4: 01-077-2879	2.7525							Bronger et al. (1996) / ICSD: 81401 / PDF-4: 04-011-4775	3.313(2)
MDyS ₂	Ohtani <i>et al.</i> (1987)/ ICSD: 44831/ PDF-4: 04-005-1430	2.685	Ohtani <i>et al.</i> (1987)/ ICSD: 44958/ PDF-4: 04-005-1451	2.734		Ballestracci (1965) / ICSD: 44946 / PDF-4: 01-089-4265	3.2255	Bronger et al. (1996) / ICSD: 81402 / PDF-4: 04-011-4776	3.310(4)	

MHoS ₂	Ohtani <i>et al.</i> (1987)/ ICSD: 44832 / PDF-4: 04-005-1431	2.6963	Ballestracci & Bertaut (1964)/ Ballestracci & Bertaut (1965)/ Brüesch & Schüler(1971) / Verheijen <i>et</i> <i>al.</i> (1975)/ ICSD: 56229 / PDF-4: 01-075-6377 / 03-065-6738	2.9384	Ballestracci (1965) / ICSD: 44947 / PDF-4: 01-089-4266	3.23	Bronger <i>et</i> <i>al.</i> (1996) / ICSD: 81403 / PDF-4: 04-011-4777	3.303(5)
2.7265	Ohtani <i>et al.</i> (1987)/ ICSD: 44959/ PDF-4: 04-005-1450	2.7058	Ballestracci & Bertaut (1964)/ [also Ballestracci & Bertaut (1965)/ Verheijen <i>et</i> <i>al.</i> (1975)]/ ICSD: 30250 /	2.9158	Ballestracci (1965) / ICSD: 44948 PDF-4: 01-074-5813/ 01-089-4267	3.2287	Bronger <i>et</i> <i>al.</i> (1996) / ICSD: 81404 / PDF-4: 04-011-4778	3.292(8)
2.7175	Ohtani <i>et al.</i> (1987)/ ICSD: 44960/ PDF-4: 04-005-1452							

						PDF-4: 01-075-0906					
MTmS ₂						Schleid & Lissner (1993)/ ICSD: 73482/ PDF-4: 01-081-2053	2.8848			Bronger <i>et al.</i> (1996) / ICSD: 81405 / PDF-4: 04-011-4779	3.302(4)
MYbS ₂						Schleid & Lissner (1993)/ ICSD: 73483/ PDF-4: 01-081-2054	2.8754	Ballestracci (1965)/ Ballestracci & Bertaut (1965) / ICSD: 44949/ PDF-4: 01-089-4268	Bronger <i>et al.</i> (1996) / ICSD: 81406 / PDF-4: 04-011-4780	3.276(2)	
MLuS ₂						Schleid & Lissner (1993)/ ICSD: 73484 / PDF-4:	2.8665	This study		Bronger <i>et al.</i> (1996) / ICSD: 81407 / PDF-4: 04-011-4781	3.293(4)
									3.154(2)		

						01-081-2055					
MYS ₂	Ohtani <i>et al.</i> (1987)/ ICSD: 44830 / PDF-4: 04-005-1433	2.7425						This study	3.1740(1 4)	This study	3.304(2)

	Reference/ ICSD/ PDF-4	Cs ⁺ -S ²⁻ (rhombohe- dral) [Å]	Reference/ ICSD/ PDF-4	Tl ⁺ -S ²⁻ (rhombohedral) [Å]
MLaS ₂	Bronger <i>et al.</i> (1993)/ ICSD: 73532 / PDF-4: 04-013-8021	3.513		
MCeS ₂	Bronger <i>et al.</i> (1993)/ ICSD: 73533 / PDF-4: 04-013-8022	3.499		
MPrS ₂	Bronger <i>et al.</i> (1993)/ ICSD: 73534 / PDF-4: 04-013-8023	3.496		
MNdS ₂	Bronger <i>et al.</i> (1993)/ ICSD:	3.469	Duczmal & Pawlak (1994) / ICSD: 54291 /	3.2837

	73535 / PDF-4: 04-013-8024		PDF-4: 01-075-6430/ 01-073-7058	
MPmS ₂				
MSmS ₂	Bronger <i>et al.</i> (1993)/ ICSD: 73536 / PDF-4: 04-013-8025	3.484		
MEuS ₂	Bronger <i>et al.</i> (1993)/ ICSD: 73537 / PDF-4: 04-013-8026	3.478		
MGdS ₂	Bronger <i>et al.</i> (1993)/ ICSD: 73538/ PDF-4: 04-013-8027	3.461	Duczmal & Pawlak (1994) / ICSD: 57323 / PDF-4: 01-073-8686	3.2846
MTbS ₂	Bronger <i>et al.</i> (1993) / ICSD: 73539/ PDF-4: 04-013-8028	3.464		
MDyS ₂	Bronger <i>et al.</i> (1993) / ICSD: 73540/	3.454	Duczmal & Pawlak (1994) / ICSD: 57244/	3.2649

	PDF-4: 04-013-8029		PDF-4: 01-073-8643	
MHoS ₂	Bronger <i>et al.</i> (1993) / ICSD: 73541 / PDF-4: 04-013-8030	3.454		
MErS ₂	Bronger <i>et al.</i> (1993) / ICSD: 73542 / PDF-4: 04-013-8031	3.457	Duczmal & Pawlak (1994)/ ICSD: 106620 / PDF-4: 01-072-8809	3.2568(19)
MTmS ₂	Bronger <i>et al.</i> (1993) / ICSD: 73543 / PDF-4: 04-013-8032	3.446		
MYbS ₂	Bronger <i>et al.</i> (1993) / ICSD: 73544 / PDF-4: 04-013-8033	3.442	Duczmal & Pawlak (1994) / ICSD: 57119 / PDF-4: 04-011-8515	3.2549
MLuS ₂	Bronger <i>et al.</i> (1993) / ICSD: 73545 / PDF-4: 04-013-8034	3.427		

Table S10 Ln^{3+} - S^{2-} distances [\AA] in selected group 1 and thallium rare-earth sulfides.

	Reference/ ICSD/ PDF-4	$\text{LiLn}^{3+}\text{-S}^{2-}$ (cubic) [\AA]	Reference/ ICSD/ PDF-4	$\text{LiLn}^{3+}\text{-S}^{2-}$ (rhombohedral) [\AA]	Reference/ ICSD/ PDF-4	$\text{NaLn}^{3+}\text{-S}^{2-}$ (cubic) [\AA]	Reference/ ICSD/ PDF-4	$\text{NaLn}^{3+}\text{-S}^{2-}$ (rhombohed ral) [\AA]	Reference/ ICSD/ PDF-4	$\text{KLn}^{3+}\text{-S}^{2-}$ (rhombohe dral) [\AA]	Referenc e/ ICSD/ PDF-4	$\text{RbLn}^{3+}\text{-S}^{2-}$ (rhombohedra l) [\AA]
MLaS_2					This study	2.9403			This study		Bronger <i>et al.</i> (1996)/ ICSD: 81394/ PDF-4: 04-011- 4782	2.9180(19)
MCeS_2					Sato <i>et al.</i> (1984)/ ICSD: 621569/ PDF-4: 04-005-1541	2.9125			Plug & Verschoor (1976)/ ICSD: 351/ PDF-4: 00-030- 0922/ 04-008- 8072		Bronger <i>et al.</i> (1996)/ ICSD: 81395 / PDF-4: 04-011- 4769	2.888(6)

MPrS ₂	Ballestracci (1965)/ Ballestracci & Bertaut (1965)/ ICSD: 44847/ PDF-4: 04-008-1008	2.843			Sato <i>et al.</i> (1984)/ ICSD: 644940	2.899			This study	2.8592(9)	Bronger <i>et al.</i> (1996) / ICSD: 81396 / PDF-4: 04-011- 4770	2.870(4)
MNdS ₂	Ballestracci (1965)/ Ballestracci & Bertaut (1965)/ ICSD: 642202/ PDF-4: 01-077-2869	2.814			Sato <i>et al.</i> (1984) / ICSD: 644912	2.8885			Verheijen <i>et al.</i> (1975)	2.8295	Bronger <i>et al.</i> (1996) / ICSD: 81397 / PDF-4: 04-011- 4771	2.855(3)
MPmS ₂												
MSmS ₂	Ballestracci (1965)/ Ballestracci & Bertaut (1965)/ ICSD: 642312	2.794			Sato <i>et al.</i> (1984)/ PDF-4: 04-005-1542	2.87			Ballestracci (1965)/ Ballestracci & Bertaut (1965)/ ICSD:	2.7647	Bronger <i>et al.</i> (1996) / ICSD: 81398 / PDF-4:	2.822(3)

								44944/ PDF-4: 01-089- 4263		04-011- 4772		
MEuS ₂	Ballestracci (1965)/ Ballestracci & Bertaut (1965)/ ICSD: 44939 / PDF-4: 04-013-3773	2.803						This study	2.8009(7)	Bronger <i>et al.</i> (1996) / ICSD: 81399 / PDF-4: 04-011- 4773	2.811(3)	
MGdS ₂	Ballestracci (1965)/ Ballestracci & Bertaut (1965) ICSD: 635897	2.765					Sato <i>et al.</i> (1984)/ ICSD:37332 / PDF:4 00-037- 1146/ 04-005-1530	2.7541	This study	2.787(2)	Bronger <i>et al.</i> (1996) / ICSD: 81400 / PDF-4: 04-011- 4774	2.8052(19)
MTbS ₂	Ballestracci (1965)/ Ballestracci & Bertaut	2.7525								Bronger <i>et al.</i> (1996) /	2.7835(19)	

	(1965)/ ICSD: 642317 / PDF-4: 01-077-2879								ICSD: 81401 / PDF-4: 04-011- 4775	
MDyS ₂	Ohtani <i>et al.</i> (1987)/ ICSD: 44831/ PDF-4: 04-005-1430			2.7684				Ballestracci (1965) / ICSD: 44946 / PDF-4: 01-089- 4265	Bronger <i>et al.</i> (1996) / ICSD: 81402 / PDF-4: 04-011- 4776	2.770(3)
MHoS ₂	Ohtani <i>et al.</i> (1987)/ ICSD: 44832 / PDF-4: 04-005-1431	2.734	Ohtani <i>et al.</i> (1987)/ ICSD: 44958/ PDF-4: 04-005-1451	2.7593		Ballestracci & Bertaut (1964)/ Ballestracci & Bertaut (1965)/ Brüesch & Schüler(1971))/ Verheijen et	2.7054	Ballestracci (1965) / ICSD: 44947 / PDF-4: 01-089- 4266	Bronger <i>et al.</i> (1996) / ICSD: 81403 / PDF-4: 04-011- 4777	2.754(5)

							<i>al.</i> (1975)/ ICSD: 56229 / PDF-4: 01-075-6377 / 03-065-6738					
M ₂ ErS ₂	Ohtani <i>et al.</i> (1987)/ 44833 / PDF-4: 04-005-1428			2.7484			Ballestracci & Bertaut (1964)/ [also Ballestracci & Bertaut (1965)/ Verheijen <i>et</i> <i>al.</i> (1975)]/ ICSD: 30250 / PDF-4: 01-075-0906	2.7272	Ballestracci (1965) / ICSD: 44948 PDF-4: 01-074- 5813/ 01-089- 4267		Bronger <i>et al.</i> (1996) / ICSD: 81404 / PDF-4: 04-011- 4778	2.750(7)
				Ohtani <i>et al.</i> (1987)/ ICSD: 44960/ PDF-4: 04-005-1452	2.7175					2.6806		
MTmS ₂							Schleid & Lissner (1993)/ ICSD: 73482/ PDF-4:	2.7147(10)		Bronger <i>et al.</i> (1996) / ICSD: 81405 /	2.741(3)	

						01-081-2053				PDF-4: 04-011- 4779	
MYbS ₂						Schleid & Lissner (1993)/ ICSD: 73483/ PDF-4: 01-081-2054	2.7072(10)	Ballestracci (1965)/ Ballestracci & Bertaut (1965) / ICSD: 44949/ PDF-4: 01-089- 4268		Bronger <i>et al.</i> (1996) / ICSD: 81406 / PDF-4: 04-011- 4780	2.7216(9)
MLuS ₂						Schleid & Lissner (1993)/ ICSD: 73484 / PDF-4: 01-081-2055	2.7000(10)	This study		Bronger <i>et al.</i> (1996) / ICSD: 81407 / PDF-4: 04-011- 4781	2.724(3)
MYS ₂	Ohtani <i>et al.</i> (1987)/	2.7425						This study	2.7552(10)	This	2.7572(18)

	ICSD: 44830 / PDF-4: 04-005-1433										study	
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	Reference/ ICSD/ PDF-4	CsLn ³⁺ -S ²⁻ (rhombohe dral) [Å] -1 st modificatio n	Reference/ ICSD/ PDF-4	Ln ³⁺ -S ²⁻ (rhombohedral) [Å]
MLaS ₂	Bronger <i>et al.</i> (1993)/ ICSD: 73532 / PDF-4: 04-013-8021	2.918(5)		
MCeS ₂	Bronger <i>et al.</i> (1993)/ ICSD: 73533 / PDF-4: 04-013-8022	2.891(8)		
MPrS ₂	Bronger <i>et al.</i> (1993)/ ICSD: 73534 / PDF-4: 04-013-8023	2.872(3)		
MNdS ₂	Bronger <i>et al.</i> (1993)/	2.847(5)	Duczmal & Pawlak (1994) /	2.7877

	ICSD: 73535 / PDF-4: 04-013-8024		ICSD: 54291 / PDF-4: 01-075-6430/ 01-073-7058	
MPmS ₂				
MSmS ₂	Bronger <i>et al.</i> (1993)/ ICSD: 73536 / PDF-4: 04-013-8025	2.826(11)		
MEuS ₂	Bronger <i>et al.</i> (1993)/ ICSD: 73537 / PDF-4: 04-013-8026	2.808(7)		
MGdS ₂	Bronger <i>et al.</i> (1993)/ ICSD: 73538/ PDF-4: 04-013-8027	2.806(4)	Duczmal & Pawlak (1994) / ICSD: 57323 / PDF-4: 01-073-8686	2.7375
MTbS ₂	Bronger <i>et al.</i> (1993) / ICSD: 73539/ PDF-4: 04-013-8028	2.789(10)		
MDyS ₂	Bronger <i>et al.</i> (1993) / ICSD: 73540/	2.762(7)	Duczmal & Pawlak (1994) / ICSD: 57244/	2.7132

	PDF-4: 04-013-8029		PDF-4: 01-073-8643	
MHoS ₂	Bronger <i>et al.</i> (1993) / ICSD: 73541/ PDF-4: 04-013-8030	2.759(3)		
MErS ₂	Bronger <i>et al.</i> (1993) / ICSD: 73542/ PDF-4: 04-013-8031	2.747(4)	Duczmal & Pawlak (1994)/ ICSD: 106620 / PDF-4: 01-072-8809	2.6925(15)
MTmS ₂	Bronger <i>et al.</i> (1993) / ICSD: 73543/ PDF-4: 04-013-8032	2.735(6)		
MYbS ₂	Bronger <i>et al.</i> (1993) / ICSD: 73544/ PDF-4: 04-013-8033	2.735(7)	Duczmal & Pawlak (1994) / ICSD: 57119 / PDF-4: 04-011-8515	2.676
MLuS ₂	Bronger <i>et al.</i> (1993) / ICSD: 73545/ PDF-4: 04-013-8034	2.713(9)		

Table S11 S²⁻-S²⁻ distances [Å] in selected group 1 and thallium rare-earth sulfides.

	Reference/ ICSD/ PDF-4	S ²⁻ -S ²⁻ (cubic) [Å]	Reference/ ICSD/ PDF-4	S ²⁻ -S ²⁻ (rhombohedral) [Å]	Reference/ ICSD/ PDF-4	S ²⁻ -S ²⁻ (cubic) [Å]	Reference/ ICSD/ PDF-4	S ²⁻ -S ²⁻ (rhomboh edral) [Å]	Reference/ ICSD/ PDF-4	S ²⁻ -S ²⁻ (rhombo edral) [Å]	Reference/ ICSD/ PDF-4	S ²⁻ -S ²⁻ (rhombo hedral) [Å]
		LiLnS ₂ (cubic)		LiLnS ₂ (rhombohedral)		NaLnS ₂ (cubic)		NaLnS ₂ (rhomboh edral)		KLnS ₂ (rhombo edral)		RbLnS ₂ (rhombo hedral)
MLaS ₂					This study	4.1582			This study		3.953(3)	Bronger <i>et al.</i> (1996)/ ICSD: 81394/ PDF-4: 04-011-4782
M CeS ₂					Sato <i>et al.</i> (1984)/ ICSD: 621569/ PDF-4: 04-005-1541	4.1189			Plug & Verschoor (1976)/ ICSD: 351/ PDF-4: 00-030- 0922/ 04-008-8072		3.904(6)	Bronger <i>et al.</i> (1996)/ ICSD: 81395 / PDF-4: 04-011-4769

	Ballestracci & Bertaut (1965)/ ICSD: 44939 / PDF-4: 04-013-3773								<i>al.</i> (1996) / ICSD: 81399 / PDF-4: 04-011-4773		
MGdS ₂	Ballestracci (1965)/ Ballestracci & Bertaut (1965) ICSD: 635897	3.9103				Sato <i>et al.</i> (1984)/ ICSD:37332 / PDF:4 00-037- 1146/ 04-005-1530	3.7667	This study	3.806(4)	Bronger <i>et al.</i> (1996) / ICSD: 81400 / PDF-4: 04-011-4774	3.819(3)
MTbS ₂	Ballestracci (1965)/ Ballestracci & Bertaut (1965)/ ICSD: 642317 / PDF-4: 01-077-2879	3.8926							Bronger <i>et al.</i> (1996) / ICSD: 81401 / PDF-4: 04-011-4775	3.788(3)	
MDyS ₂	Ohtani <i>et al.</i> (1987)/ ICSD: 44831/ PDF-4: 04-005-1430	3.8665	Ohtani <i>et al.</i> (1987)/ ICSD: 44958/ PDF-4: 04-005-1451	3.6947				Ballestracci (1965) / ICSD: 44946 / PDF-4:	Bronger <i>et al.</i> (1996) / ICSD: 81402 / PDF-4:	3.771(5)	

								01-089-4265		04-011-4776	
MHoS ₂	Ohtani <i>et al.</i> (1987)/ ICSD: 44832 / PDF-4: 04-005-1431		3.7325			Ballestracci & Bertaut (1964)/ Ballestracci & Bertaut (1965)/ Brüesch & Schüler(1971))/ Verheijen <i>et</i> <i>al.</i> (1975)/ ICSD: 56229 /	3.699	Ballestracci (1965) / ICSD: 44947 /	3.6033	Bronger <i>et</i> <i>al.</i> (1996) / ICSD: 81403 /	3.748(7)
		Ohtani <i>et al.</i> (1987)/ ICSD: 44959/ PDF-4: 04-005-1450	3.8559			PDF-4: 01-075-6377 /		01-089-4266	PDF-4: 04-011-4777		
MErS ₂	Ohtani <i>et al.</i> (1987)/ 44833 / PDF-4: 04-005-1428		3.881			Ballestracci & Bertaut (1964)/ [also Ballestracci & Bertaut (1965)/ Verheijen <i>et</i>	3.7728	Ballestracci (1965) / ICSD: 44948 /	3.5776	Bronger <i>et</i> <i>al.</i> (1996) / ICSD: 81404 /	3.747(11)
		Ohtani <i>et al.</i> (1987)/ ICSD: 44960/ PDF-4: 04-005-1452	3.8431			PDF-4: 01-074- 5813/ 01-089-4267			04-011-4778		

							<i>al.</i> (1975)]/ ICSD: 30250 / PDF-4: 01-075-0906					
MTmS ₂							Schleid & Lissner (1993)/ ICSD: 73482/ PDF-4: 01-081-2053	3.761(2)			<i>Bronger et</i> <i>al.</i> (1996) / ICSD: 81405 / PDF-4: 04-011-4779	3.727(5)
MYbS ₂							Schleid & Lissner (1993)/ ICSD: 73483/ PDF-4: 01-081-2054	3.755(2)	Ballestracci (1965)/ Ballestracci & Bertaut (1965) / ICSD: 44949/ PDF-4: 01-089-4268	3.5549	<i>Bronger et</i> <i>al.</i> (1996) / ICSD: 81406 / PDF-4: 04-011-4780	3.715(3)
MLuS ₂							Schleid & Lissner	3.748(2)	This study	3.714(4)	<i>Bronger et</i> <i>al.</i> (1996) /	3.709(5)

						(1993)/ ICSD: 73484 / PDF-4: 01-081-2055				ICSD: 81407 / PDF-4: 04-011-4781	
MYS ₂	Ohtani <i>et al.</i> (1987)/ ICSD: 44830 / PDF-4: 04-005-1433	3.8785					This study	3.767(2)	This study	3.749(4)	

	Reference/ ICSD/ PDF-4	S ²⁻ -S ²⁻ (rhomboh edral) [Å]	Reference/ ICSD/ PDF-4	S ²⁻ -S ²⁻ (rhombohedral) [Å]
		CsLnS ₂		TlLnS ₂
MLaS ₂	Bronger <i>et al.</i> (1993)/ ICSD: 73532 / PDF-4: 04-013-8021	3.942(11)		
MCeS ₂	Bronger <i>et al.</i> (1993)/ ICSD: 73533 / PDF-4: 04-013-8022	3.906(16)		
MPrS ₂	Bronger <i>et al.</i> (1993)/	3.883(5)		

	ICSD: 73534 / PDF-4: 04-013-8023			
MNdS ₂	Bronger <i>et al.</i> (1993)/ ICSD: 73535 / PDF-4: 04-013-8024	3.855(8)	Duczmal & Pawlak (1994) / ICSD: 54291 / PDF-4: 01-075-6430/ 01-073-7058	3.7464
MPmS ₂				
MSmS ₂	Bronger <i>et al.</i> (1993)/ ICSD: 73536 / PDF-4: 04-013-8025	3.83(2)		
MEuS ₂	Bronger <i>et al.</i> (1993)/ ICSD: 73537 / PDF-4: 04-013-8026	3.797(13)		
MGdS ₂	Bronger <i>et al.</i> (1993)/ ICSD: 73538/ PDF-4: 04-013-8027	3.814(8)	Duczmal & Pawlak (1994) / ICSD: 57323 / PDF-4: 01-073-8686	3.6863
MTbS ₂	Bronger <i>et al.</i> (1993) /	3.78(2)		

	ICSD: 73539/ PDF-4: 04-013-8028			
MDyS ₂	Bronger <i>et al.</i> (1993) / ICSD: 73540/ PDF-4: 04-013-8029	3.748(14)	Duczmal & Pawlak (1994) / ICSD: 57244/ PDF-4: 01-073-8643	3.6691
MHoS ₂	Bronger <i>et al.</i> (1993) / ICSD: 73541/ PDF-4: 04-013-8030	3.742(6)		
MErS ₂	Bronger <i>et al.</i> (1993) / ICSD: 73542/ PDF-4: 04-013-8031	3.723(8)	Duczmal & Pawlak (1994)/ ICSD: 106620 / PDF-4: 01-072-8809	3.648(2)
MTmS ₂	Bronger <i>et al.</i> (1993) / ICSD: 73543/ PDF-4: 04-013-8032	3.706(13)		
MYbS ₂	Bronger <i>et al.</i> (1993) / ICSD: 73544/ PDF-4: 04-013-8033	3.708(11)	Duczmal & Pawlak (1994) / ICSD: 57119 / PDF-4: 04-011-8515	3.6277
MLuS ₂	Bronger <i>et al.</i> (1993) /	3.688(19)		

	ICSD: 73545/ PDF-4: 04-013-8034			
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Table S12 Bond valence sums of the constituting ions in selected Li rare-earth sulfides. (Hypothetic structures are considered as cubic of the disordered NaCl type with the same volume of the unit cell as the corresponding ones of the α -NaFeO₂ structural type.)

	Bertaut (1965)	04-013-3773											
LiGdS ₂	Ballestracci (1965)/ Ballestracci & Bertaut (1965)	ICSD: 635897	0.649	3.197	1.923								
LiTbS ₂	Ballestracci (1965)	ICSD: 642317/ PDF-4: 01-077- 2879	0.668	3.115	1.892	PDF-4 04-007- 9874					0.669	3.123	1.896
LiDyS ₂	Ohtani <i>et al.</i> (1987)	ICSD: 44831/ PDF-4: 04-005- 1430	0.702	2.939	1.821	Ohtani <i>et al.</i> (1987)	44958	0.801	2.678	1.740	0.718	3.008	1.863
LiHoS ₂	Ohtani <i>et al.</i> (1987)	ICSD: 44832/ PDF-4: 04-005- 1431	0.716	3.082	1.899	Ohtani <i>et al.</i> (1987)	44959	0.777	2.820	1.798	0.715	3.078	1.896
LiErS ₂	Ohtani <i>et al.</i> (1987)	ICSD: 44833 / PDF-4: 04-005- 1428	0.734	2.992	1.863	Ohtani <i>et al.</i> (1987)	44960	0.757	2.752	1.754	0.716	2.920	1.818
LiTmS ₂						Tromme (1971)					0.781	3.102	1.942

LiYbS ₂					Ballestracci (1965)					0.763	2.868	1.816
LiLuS ₂					Tromme (1971)					0.789	2.970	1.878
LiYS ₂	Ohtani <i>et al.</i> (1987)	ICSD: 44957 / PDF-4: 04-005- 1449	0.686	2.951	1.819	Ohtani <i>et al.</i> (1987)				0.708	3.049	1.879

Table S13 Bond valence sums of the constituting ions in selected Na rare-earth sulfides. (Hypothetic structures are considered as cubic of the disordered NaCl type with the same volume of the unit cell as the corresponding ones of the $\alpha\text{-NaFeO}_2$ structural type.)

		1539											
NaNdS ₂	Sato <i>et al.</i> (1984)	ICSD: 644912	1.159	2.678	1.918	Sato <i>et al.</i> (1984)					1.150	2.659	1.905
NaPmS ₂													
NaSmS ₂	Sato <i>et al.</i> (1984)	PDF-4: 04-005-1542	1.217	2.526	1.872	Sato <i>et al.</i> (1984)	PDF-4: 04-005-1537				1.204	2.499	1.852
NaEuS ₂						Ballestracci & Bertaut (1964) / Ballestracci & Bertaut (1965)/					1.241	2.439	1.840
NaGdS ₂						Sato <i>et al.</i> (1984)	ICSD: 37332/ PDF-4: 00-037-1146/ PDF-4: 04-005-1530	0.947	3.274	2.111	1.275	2.506	1.891
NaTbS ₂						Sato <i>et al.</i> (1984)	PDF-4: 04-005-1536				1.317	2.453	1.885
NaDyS ₂						Sato <i>et al.</i> (1984)	PDF-4: 04-005-1531				1.346	2.249	1.798
NaHoS ₂						Ballestracci & Bertaut (1964)/ Ballestracci &	ICSD: 56229/ PDF-4: 01-075-	1.012	3.263	2.138	1.413	2.426	1.920

					Bertaut (1965)/ Ballestracci & Bertaut (1964)	6377 ICSD: 30250/ PDF-4: 01-075- 0906	1.076	2.915	1.995	1.402	2.281	1.842
NaErS ₂					Schleid & Lissner (1993)	ICSD: 73482 / PDF-4: 01-081- 2053	1.1703	2.934	2.052	1.492	2.363	1.928
NaYbS ₂					Schleid & Lissner (1993)	ICSD: 73483/ PDF-4: 01-081- 2054	1.2004	2.8360	2.018	1.527	2.290	1.909
NaLuS ₂					Schleid & Lissner (1993)	ICSD: 73484 / PDF-4: 01-081- 2055	1.2294	2.8920	2.0610	1.561	2.341	1.951
NaYS ₂					Ballestracci & Bertaut (1964)/Brüesch & Schüler (1971)	ICSD: 76543 / PDF-4: 01-089- 5281				1.367	2.347	1.857

Table S14 Bond valence sums of the constituting ions in selected K rare-earth sulfides. (Hypothetic structures are considered as cubic of the disordered NaCl type with the same volume of the unit cell as the corresponding ones of the α -NaFeO₂ structural type.)

Compound	reference	ICSD/ PDF-4	b.v. K(cub)	b.v. Ln(cub)	b.v. S(cub)	reference	ICSD/ PDF-4	b.v. K (rhomb)	b.v. Ln(rhomb)	b.v. S(rhomb)	b.v. K (hypot)	b.v. Ln(hypot)	b.v. S(hypot)
KLaS ₂						This study		1.030	2.911	1.971	1.662	1.902	1.782
KCeS ₂						Plug & Verschoor (1976)	ICSD: 351/ PDF-4: 00-030- 0922/ 04- 008-8072	1.074	2.993	2.033	1.773	1.923	1.848
KPrS ₂						This study		1.0866	2.978	2.032	1.8340	1.8840	1.8590
KNdS ₂						Verheijen <i>et al.</i> (1975)		1.1041	3.141	2.1225	1.933	1.933	1.933
KPmS ₂													
KSmS ₂						Ballestracci (1965)/ Ballestracci & Bertaut (1965)	ICSD: 44944 / PDF-4: 01-089- 4263	1.0410	3.368	2.204	2.0850	1.8720	1.9790
KEuS ₂						This study		1.189	2.885	2.037	2.093	1.780	1.937
KGdS ₂						This study		1.192	2.997	2.095	2.148	1.827	1.988
KTbS ₂						Ballestracci (1965)/				2.216	1.785	2.000	

					Ballestracci & Bertaut (1965)								
KDyS ₂					Ballestracci (1965)/ Ballestracci & Bertaut (1965)	ICSD: 44946 / PDF-4: 01-089- 4265	1.0770	3.0810	2.0790	2.289	1.655	1.972	
KHoS ₂					Ballestracci (1965)	ICSD: 44947/ PDF-4: 01-089- 4266	1.0640	3.3630	2.2130	2.3580	1.7510	2.0550	
KErS ₂					Ballestracci (1965)/ Ballestracci & Bertaut (1965)	ICSD: 44948/ PDF-4: 01-074- 5813/ 01-089- 4267	1.071	3.316	2.193	2.419	1.702	2.061	
KTmS ₂					Tromme (1971)	PDF-4: 04-001- 8391				2.449	1.678	2.064	
KYbS ₂					Ballestracci (1965)	ICSD: 44949 / PDF-4: 01-089- 4268	1.073	3.213	2.143	2.4990	1.6220	2.0610	
KLuS ₂					This study		1.306	2.812	2.059	2.533	1.644	2.088	

KYS ₂						This study		1.238	2.852	2.045	2.298	1.707	2.003
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Table S15 Bond valence sums of the constituting ions in selected Rb rare-earth sulfides. (Hypothetic structures are considered as cubic of the disordered NaCl type with the same volume of the unit cell as the corresponding ones of the α -NaFeO₂ structural type.)

Compound	reference	ICSD/ PDF-4	b.v. Rb(cub)	b.v. Ln(cub)	b.v. S(cub)	reference	ICSD/ PDF-4	b.v. Rb(rhomb)	b.v. Ln(rhomb)	b.v. S(rhomb)	b.v. Rb(hypot)	b.v. Ln(hypot)	b.v. S(hypot)
RbLaS ₂						Bronger <i>et al.</i> (1996)	ICSD: 81394/ PDF-4: 04-011- 4782	0.976	2.831	1.903	1.8972	1.6132	1.7553
RbCeS ₂						Bronger <i>et al.</i> (1996)	ICSD: 81395/ PDF-4: 04-011- 4769	1.031	2.904	1.968	2.0381	1.6418	1.84
RbPrS ₂						Bronger <i>et al.</i> (1996)	ICSD: 81396/ PDF-4: 04-011- 4770	1.034	2.890	1.962	2.1024	1.6045	1.8536
RbNdS ₂						Bronger <i>et al.</i> (1996)	ICSD: 81397/	1.057	2.935	1.996	2.1806	1.6198	1.9003

						PDF-4: 04-011- 4771						
RbPmS ₂												
RbSmS ₂					Bronger <i>et al.</i> (1996)	ICSD: 81398/ 04-011- 4772	1.094	2.878	1.986	2.3361	1.5575	1.9469
RbEuS ₂					Bronger <i>et al.</i> (1996)	ICSD: 81399/ PDF-4: 04-011- 4773	1.104	2.804	1.964	2.3872	1.5078	1.9476
RbGdS ₂					Bronger <i>et al.</i> (1996)	ICSD: 81400/ PDF-4: 04-011- 4774	1.126	2.852	1.989	2.4361	1.5387	1.9875
RbTbS ₂					Bronger <i>et al.</i> (1996)	ICSD: 81401/ PDF-4: 04-011- 4775	1.145	2.865	2.005	2.5403	1.5201	2.0303
RbDyS ₂					Bronger <i>et al.</i> (1996)	ICSD: 81402/ PDF-4: 04-011- 4776	1.153	2.663	1.908	2.6064	1.3998	2.0032

RbHoS ₂					Bronger <i>et al.</i> (1996)	ICSD: 81403/ PDF-4: 04-011- 4777	1.177	2.860	2.018	2.7032	1.4916	2.0975
RbErS ₂					Bronger <i>et al.</i> (1996)	ICSD: 81404/ 04-011- 4778	1.211	2.741	1.976	2.7549	1.4401	2.0976
RbTmS ₂					Bronger <i>et al.</i> (1996)	ICSD: 81405/ PDF-4: 04-011- 4779	1.180	2.734	1.957	2.766	1.4074	2.0868
RbYbS ₂					Bronger <i>et al.</i> (1996)	ICSD: 81406/ 04-011- 4780	1.264	2.695	1.979	2.9157	1.4055	2.1607
RbLuS ₂					Bronger <i>et al.</i> (1996)	ICSD: 81407/ PDF-4: 04-011- 4781	1.207	2.709	1.958	2.8766	1.3866	2.1317
RbYS ₂					This study		1.171	2.836	2.004	2.681	1.480	2.081

Table S16 Bond valence sums of the constituting ions in selected CsLnS_2 structures of $\alpha\text{-NaFeO}_2$ structural family and the hypothetic cubic structures.
 (Hypothetic structures are considered as cubic of the disordered NaCl type with the same volume of the unit cell as the corresponding ones of the $\alpha\text{-NaFeO}_2$ structural type.)

Compound	reference	ICSD/ PDF-4	b.v. $\text{Cs}(\text{cub})$	b.v. $\text{Ln}(\text{cub})$	b.v. $\text{S}(\text{cub})$	reference	ICSD/ PDF-4	b.v. $\text{Cs}(\text{rhomb})$	b.v. $\text{Ln}(\text{rhomb})$	b.v. $\text{S}(\text{rhomb})$	b.v. $\text{Cs}(\text{hypot})$	b.v. $\text{Ln}(\text{hypot})$	b.v. $\text{S}(\text{hypot})$
CsLaS_2						Bronger <i>et al.</i> (1993)	ICSD: 73532/ PDF-4: 04-013-8021	1.113	2.831	1.972	1.390	2.732	2.061
CsCeS_2						Bronger <i>et al.</i> (1993)	ICSD: 73533/ PDF-4: 04-013-8022	1.157	2.890	2.020	1.401	2.907	2.154
CsPrS_2						Bronger <i>et al.</i> (1993)	ICSD: 73534/ PDF-4: 04-013-8023	1.167	2.879	2.023	1.377	3.015	2.196
CsNdS_2						Bronger <i>et al.</i> (1993)	ICSD: 73535/ PDF-4: 04-013-8024	1.254	2.996	2.125	1.440	3.239	2.340
CsPmS_2													
CsSmS_2						Bronger <i>et al.</i> (1993)	ICSD: 73536/ PDF-4: 04-013-8025	1.200	2.850	2.020	1.320	3.310	2.315
CsEuS_2						Bronger <i>et al.</i> (1993)	ICSD: 73537/ PDF-4: 04-013-8026	1.224	2.830	2.028	1.299	3.438	2.369
CsGdS_2						Bronger <i>et al.</i> (1993)	ICSD: 73538/ PDF-4: 04-013-8027	1.283	2.848	2.066	1.335	3.532	2.433
CsTbS_2						Bronger <i>et al.</i>	ICSD: 73539/	1.270	2.830	2.050	1.294	3.614	2.454

					(1993)	PDF-4: 04-013-8028							
CsDyS ₂					Bronger <i>et al.</i> (1993)	ICSD: 73540/ PDF-4: 04-013-8029	1.305	2.720	2.015	1.232	3.836	2.534	
CsHoS ₂					Bronger <i>et al.</i> (1993)	ICSD: 73541/ PDF-4: 04-013-8030	1.306	2.826	2.066	1.273	3.856	2.565	
CsErS ₂					Bronger <i>et al.</i> (1993)	ICSD: 73542/ PDF-4: 04-013-8031	1.298	2.764	2.031	1.229	3.930	2.580	
CsTmS ₂					Bronger <i>et al.</i> (1993)	ICSD: 73543/ PDF-4: 04-013-8032	1.336	2.780	2.058	1.234	4.054	2.644	
CsYbS ₂					Bronger <i>et al.</i> (1993)	ICSD: 73544/ PDF-4: 04-013-8033	1.350	2.630	1.990	1.174	4.071	2.622	
CsLuS ₂					Bronger <i>et al.</i> (1993)	ICSD: 73545/ PDF-4: 04-013-8034	1.406	2.790	2.100	1.242	4.308	2.775	

Table S17 Bond valence sums of the constituting ions in selected CsLnS₂ structures of *P6₃/mmc* structural type. (Hypothetic structures are considered as cubic of the disordered NaCl type with the same volume of the unit cell as those of the pertinent hexagonal modifications.)

Compound	reference	ICSD/ PDF-4	b.v. Cs(cub)	b.v. Ln(cub)	b.v. S(cub)	reference	ICSD/ PDF-4	b.v. Cs(rhomb)	b.v. Ln(rhomb)	b.v. S(rhomb)	b.v. Cs(hypot)	b.v. Ln(hypot)	b.v. S(hypot)
CsLaS ₂						Bronger <i>et al.</i> (1993)							
CsCeS ₂						Bronger <i>et al.</i> (1993)							
CsPrS ₂						Bronger <i>et al.</i> (1993)	ICSD: 73548/ PDF-4: 04-013-8035	1.149	2.898	2.023	3.015	1.377	2.196000
CsNdS ₂						Bronger <i>et al.</i> (1993)	ICSD: 602832/ PDF-4: 01-079-9425				3.124	1.389	2.256000
CsPmS ₂													
CsSmS ₂						Bronger <i>et al.</i> (1993)	ICSD: 602833/ PDF-4: 01-079-9426				3.356	1.339	2.347000
CsEuS ₂						Bronger <i>et al.</i> (1993)	ICSD: 602834/ PDF-4: 01-079-9427				3.480	1.315	2.398000

CsGdS ₂					Bronger <i>et al.</i> (1993)	ICSD: 602861/ PDF-4: 01-079-9430				3.556	1.344	2.450000
CsTbS ₂					Bronger <i>et al.</i> (1993)	ICSD: 602889/ PDF-4: 01-079-9436				3.624	1.298	2.461000
CsDyS ₂					Bronger <i>et al.</i> (1993)	ICSD: 602845/ PDF-4: 01-079-9429				3.846	1.236	2.541000
CsHoS ₂					Bronger <i>et al.</i> (1993)	ICSD: 602874/ PDF-4: 01-079-9431				3.873	1.279	2.576000
CsErS ₂					Bronger <i>et al.</i> (1993)	ICSD: 602875/ PDF-4: 01-079-9432				3.925	1.228	2.577000
CsTmS ₂					Bronger <i>et al.</i> (1993)	ICSD: 602876/ PDF-4: 01-079-9433				4.071	1.240	2.655000
CsYbS ₂					Bronger <i>et al.</i> (1993)	ICSD: 603271/ PDF-4:				4.082	1.177	2.630000

							01-079-9508							
CsLuS ₂						Bronger <i>et al.</i> (1993)	ICSD: 602878/ PDF-4: 01-079-9435					4.303	1.241	2.772000

Table S18 Bond valence sums of the constituting ions in selected Tl rare-earth sulfides. (Hypothetic structures are considered as cubic or the disordered NaCl type with the same volume of the unit cell as the corresponding ones of the α -NaFeO₂ structural type.)

Compound	reference	ICSD/ PDF-4	b.v. Tl(cub)	b.v. Ln(cub)	b.v. S(cub)	reference	ICSD/ PDF-4	b.v. Tl(rhomb)	b.v. Ln(rhomb)	b.v. S(rhomb)	b.v. Tl(hypot)	b.v. Ln(hypot)	b.v. S(hypot)	
TlLaS ₂														
TlCeS ₂														
TlPrS ₂														
TlNdS ₂						Duczmal & Pawlak (1994)	ICSD: 54291/ PDF-4: 01-075- 6430/ PDF-4: 01-073- 7058	1.025	3.516	2.271	2.133	1.915	2.024	
TlPmS ₂														
TlSmS ₂						Kabré <i>et al.</i> (1974)	PDF-4: 04-002- 0535				2.122	1.709	1.916	

TlEuS ₂					Kabré <i>et al.</i> (1974)	ICSD: 631635				2.128	1.624	1.876
TlGdS ₂					Duczmal & Pawlak (1994)	57323	1.022	3.424	2.223	2.323	1.773	2.048
TlTbS ₂					Kabré <i>et al.</i> (1974)					2.264	1.637	1.951
TlDyS ₂					Duczmal & Pawlak (1994)	ICSD: 57244/ PDF-4: 01-073- 8643	1.078	3.109	2.094	2.479	1.608	2.044
TlHoS ₂					Kabré <i>et al.</i> (1974)					2.332	1.555	1.944
TlErS ₂					Duczmal & Pawlak (1994)	ICSD: 106620/ PDF-4: 01-072- 8809	1.103	3.201	2.152	2.610	1.648	2.129
TlTmS ₂					Kabré <i>et al.</i> (1974)					2.409	1.481	1.945
TlYbS ₂					Duczmal & Pawlak (1994)	ICSD: 57119/ PDF-4: 04-011- 8515	1.108	3.085	2.097	2.677	1.559	2.118
TlLuS ₂					Kabré <i>et al.</i> (1974)					2.485	1.447	1.967

TlYS ₂						Kabré <i>et al.</i> (1974)							2.329	1.553	1.941
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Figure S1 Comparison of c/a for selected rhombohedral (Cs(I)) and hexagonal modifications of $\text{Cs}^+Ln^{3+}\text{S}_2$ (Cs(II)). The structures are referenced in deposited Table 4.

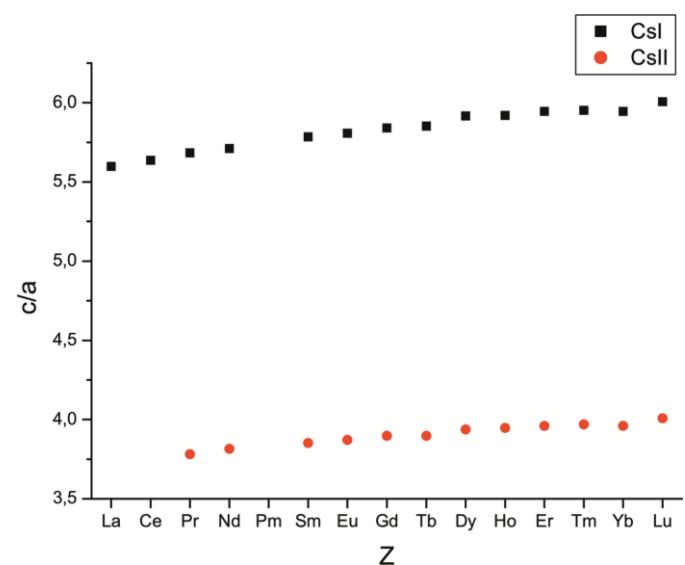


Figure S2 Comparison of scaled c/a for selected rhombohedral (Cs(I)) and hexagonal modifications of $\text{Cs}^+ \text{Ln}^{3+} \text{S}_2$ (Cs(II)). The structures are referenced in deposited Table 4.

