

**substance:  $\text{La}_2\text{S}_3$**

**property: crystal structure, physical properties**

**$\alpha\text{-La}_2\text{S}_3$**

**crystal structure** orthorhombic ( $\text{D}_{2h}^{16} - \text{Pnma}$ )

**lattice parameters**

$a$	7.584 Å	68S
	7.587(7) Å	81G
$b$	15.860 Å	68S
	15.863(4) Å	81G
$c$	4.144 Å	68S
	4.149(2) Å	81G

**melting point**

$T_m$	1950°C	81G
-------	--------	-----

**Debye temperature**

$\Theta_D$	317(1) K	81G
------------	----------	-----

**heat capacity:** Fig. 1

**$\beta\text{-La}_2\text{S}_3$**

**crystal structure** tetragonal ( $\text{D}_{4h}^{20} - \text{I4}_1/\text{acd}$ )

$a = b$	15.62 Å	73B
	15.65(4) Å	81G
$c$	20.62 Å	73B
	20.64(6) Å	81G

**energy gap**

$E_g$	2.58 eV	direct	optical determination	80L
	2.6 eV	direct	fundamental absorption edge	81S
	1.38 eV		indirect or impurity tail	80L

**resistivity**

$\rho$	$2 \cdot 10^{12} \dots 4 \cdot 10^{14} \Omega \text{ cm}$	82A
--------	---	-----

*Figures and further references for  $\beta$ -La<sub>2</sub>S<sub>3</sub>:*

**phase transition**  $\beta \rightarrow \gamma$  at 1300°C

**heat capacity:** Fig. 2; for heat capacity, enthalpy and entropy, see also [69P]

**optical spectra** for Nd-doped crystals: Figs. 3, 4; optical spectra for Nd, Ce-codoped crystals: Figs. 5, 6, 7

**photoconductivity** of a Ce-doped crystal: Fig. 8

**photoluminescence, cathodoluminescence** of a Ce-doped crystal: Figs. 9, 10

### $\gamma$ -La<sub>2</sub>S<sub>3</sub>

**crystal structure** cubic (Th<sub>3</sub>P<sub>4</sub>-defect structure, T<sub>d</sub><sup>6</sup> – I $\bar{4}$  3d)

#### **lattice parameters**

$a$	8.723 Å	85Z
	8.726(1) Å	78K
	8.731 Å	60P
	8.7253(8) Å	76K
	8.725 Å	81K
	8.69 Å	80K

#### **melting point**

$T_m$	2080°C	60P
	1980(30)°C	76K,
		81K
	2100°C	80K

#### **density**

$d$	4.93 g cm <sup>-3</sup>	60P
-----	-------------------------	-----

#### **linear thermal expansion coefficient**

$\alpha$	9.9·10 <sup>-6</sup> K <sup>-1</sup>	66D
----------	--------------------------------------	-----

#### **energy gap and other energy parameters**

$E_g$	2.76 ± 0.1 eV	optical energy gap	85Z
	2.8 ± 0.25 eV	thermodynamic	85Z
	1.9 eV	X-ray spectra	83S
	2.9 eV	optical gap	80K
	2.4 eV	optical gap	82B,
			81B
	2.8(1) eV	optical gap	79Z
$dE_g/dT$	4.9·10 <sup>-4</sup> eV/K	$T = 250 \text{ K} \dots 350 \text{ K}$	79Z

$E_b$	4.8 eV	S 3p-level	MgK $\alpha$ XPS, Fig. 24 ( $E_b$ rel. to $E_F$ )	91K
	13.6 eV	S 3s-level	MgK $\alpha$ XPS, Fig. 24	
	18.9 eV	La 5p $_{3/2}$ -level	MgK $\alpha$ XPS, Fig. 24	
	20.9 eV	La 5p $_{1/2}$ -level	MgK $\alpha$ XPS, Fig. 24	
	36 eV	La 5s-level	MgK $\alpha$ XPS, Fig. 25	
	103 eV	La 4d $_{5/2}$ -level	MgK $\alpha$ XPS, Fig. 25	
	104 eV	La 4d $_{3/2}$ -level	MgK $\alpha$ XPS, Fig. 25	
	197 eV	La 4p $_{3/2}$ -level	MgK $\alpha$ XPS	
	209 eV	La 4p $_{1/2}$ -level	MgK $\alpha$ XPS	
	834 eV	La 3d $_{5/2}$ -level	AlK $\alpha$ XPS, Fig. 26	
	851 eV	La 3d $_{3/2}$ -level	AlK $\alpha$ XPS, Fig. 26	
$E$	5.9 eV	S 3p- $E_F$	ELS, Fig. 27	91K
	11.1 eV	S 3p-cond. band, surface plasmon	ELS, Fig. 27	
	16.1 eV	bulk plasmon	ELS, Fig. 27	
	20.8 eV	La 5p- $E_F$	ELS, Fig. 27	
	27.5 eV	La 5p-5d	ELS, Fig. 27	
	$\approx 37$ eV	La 5s- $E_F$	ELS, Fig. 27	
	118 eV	La 4d-4f	ELS, Fig. 28	
			reflectivity: Fig. 29	

#### thermal conductivity

$\kappa$	$2.3 \cdot 10^{-2} \text{ W cm}^{-1} \text{ K}^{-1}$	72G
----------	--	-----

#### Debye temperature

$\Theta_D$	320 K	72S
	285 K	81G

#### phonon wavenumbers

$(\nu/c)_{TO}$	195 $\text{cm}^{-1}$	$(\nu/c)$ from Raman spectrum	79A
	230 $\text{cm}^{-1}$		
$(\nu/c)_{LO}$	301 $\text{cm}^{-1}$		

#### dielectric constants

$\epsilon(0)$	17.2	79A
$\epsilon(\infty)$	7.0	79A, 79Z

#### refractive index

$n$	2.6	$\lambda = 1...15 \mu\text{m}$	80K
	2.8	$\lambda = 0.55 \mu\text{m}$	

#### electrical conductivity

$\sigma$	$10^{-10} \Omega^{-1} \text{ cm}^{-1}$	80K
	$10^{-9}...10^{-10} \Omega^{-1} \text{ cm}^{-1}$	79Z
	$0.7 \cdot 10^{-12} \Omega^{-1} \text{ cm}^{-1}$	81B
	$10^{-12} \Omega^{-1} \text{ cm}^{-1}$ $T = 145 \text{ K}$	82B

Further figures and references for  $\gamma\text{-La}_2\text{S}_3$ :

**phase diagram:** Fig. 11

**coordination polyhedra:** Fig. 12

**Raman spectrum:** Figs. 13, 14

**absorption and transmission spectra:** Figs. 14, 15, 16

real and imaginary part of the **dielectric constant**: Fig. 17

**reflectivity spectrum**: Fig. 18

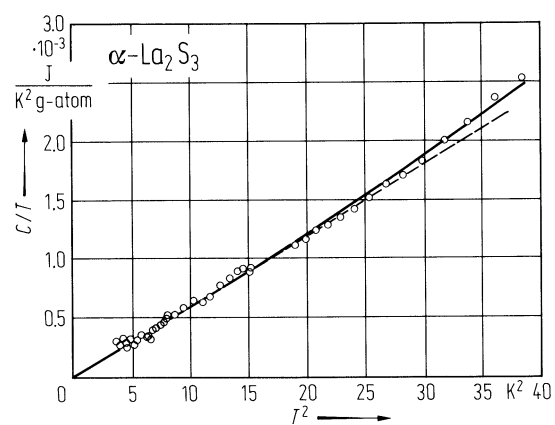
**luminescence** and absorption of Nd-doped crystals: Figs. 19...23

## References:

- 60P Picon, M., Domange, L., Flahaut, J., Guittard, M., Patrie, M.: Bull. Soc. Chim. Fr. 2 (1960) 221.
- 66D Dudnik, E. M., Lashkarev, G. V., Paderno, Y. B., Obolonchik, V. A.: Inorg. Mater. 2 (1966) 833.
- 66H Holtzberg, F., Methfessel, S.: J. Appl. Phys. 37 (1966) 1433.
- 67B Berkooz, O., Malamud, M., Shtrikman, S.: Solid State Commun. 6 (1967) 185.
- 68S Sleight, A. W., Prewitt, C. T.: Inorg. Chem. 7 (1968) 2282.
- 69P Pankov, I. E., Nogteva, V. V., Yarembash, E. I.: Russ. J. Phys. Chem. 43 (1969) 1316.
- 72G Goryachev, Yu. M., Kutsenok, T. G.: High Temp. High Press. 4 (1972) 663.
- 72S Smirnov, I. A.: Phys. Status Solidi (a) 14 (1972) 363.
- 73B Besancon, P.: J. Solid State Chem. 7 (1973) 232.
- 76K Kamarzin, A. A., Sokolov, V. V., Mironov, K. E., Maloviikii, N., Vasileva, I. G.: Mater. Res. Bull. 11 (1976) 695.
- 78K Konstantinov, V. L., Skorniyakov, G. P., Kamarzin, A. A., Sokolov, V. V.: Inorg. Mater. 14 (1978) 659.
- 79A Arkatova, T. G., Zhuze, V. P., Karin, M. G., Kamarzin, A. A., Kukharskii, A. A., Mikhailov, B. A., Shelykh, A. I.: Sov. Phys. Solid State 21 (1979) 1979.
- 79Z Zhuze, V. P., Kamarzin, A. A., Karin, M. G., Sidorin, K. K., Shelykh, A. I.: Sov. Phys. Solid State 21 (1979) 1968.
- 80K Kaminskii, A. A., Sarkisov, C. E., Chan Niok, Denisenko, G. A., Kamarzin, A. A., Sokolov, V. V., Klypin, V. V., Maloviikii, Yu. N.: Izv. Akad. Nauk SSSR, Neorg. Mater. 16 (1980) 1333.
- 80L Leiss, M.: J. Phys. C 13 (1980) 151.
- 81B Batirov, T. M., Fridkin, V. M., Kamarzin, A. A., Malovitskii, Y. I., Verkhovskaya, K. A.: Phys. Status Solidi (a) 65 (1981) K163.
- 81G Gschneidner, K. A., Beaudry, B. J., Takeshita, T., Eucker, S. S., Taher, S. M. A., Ho, J. C., Gruber, J. B.: Phys. Rev. B 24 (1981) 7187.
- 81K Kamarzin, A. A., Mironov, K. E., Sokolov, V. V., Malovitskii, Y. N., Vasil'yeva, I. G.: J. Cryst. Growth 52 (1981) 619.
- 81S Scharmer, E. G., Leiß, M., Huber, G.: J. Lumin. 24/25 (1981) 751.
- 82A Astalleva, L. V., Skorniyakov, G. P., Kamarzin, A. A., Malovitskii, Y. N.: Sov. Phys. Solid State 24 (1982) 367.
- 82B Batirov, T. M., Verkhovskaya, K. A., Kamarzin, A. A., Malovitskii, Y. N., Lisoivan, V. I., Fridkin, V. M.: Sov. Phys. Solid State 24 (1982) 746.
- 82S Scharmer, E. G., Leiß, M., Huber, G.: J. Phys. C 15 (1982) 1071.
- 83B Balabanova, L. A., Zhuze, V. P., Ostroumova, E. G., Shul'man, S. G.: Sov. Phys. Solid State 25(6) (1983) 971.
- 83K1 Kamarzin, A. A., Mamedov, A. A., Smirnov, V. A., Sobol', A. A., Sokolov, V. V., Shcherbakov, I. A.: Sov. J. Quantum Electron. 13 (1983) 1027.
- 83K2 Kamarzin, A. A., Mamedov, A. A., Smirnov, V. A., Sokolov, V. V., Shcherbakov, I. A.: Sov. J. Quantum Electron. 13 (1983) 328.
- 83S Soldatov, A. V., Gusatinskii, A. N., Karin, M. G., Sidorin, K. K., Sadovskaya, O. A.: Inorg. Mater. 19 (1983) 951-954.
- 85Z Zhuze, V. P., Karin, M. G., Sidorin, K. K., Sokolov, V. V., Shelykh, A. I.: Sov. Phys. Solid State 27(12) (1985) 2205.
- 91K Kaciulis, S., Latisenka, A., Plesanovas A.: Surf. Sci. 251/252 (1991) 330.

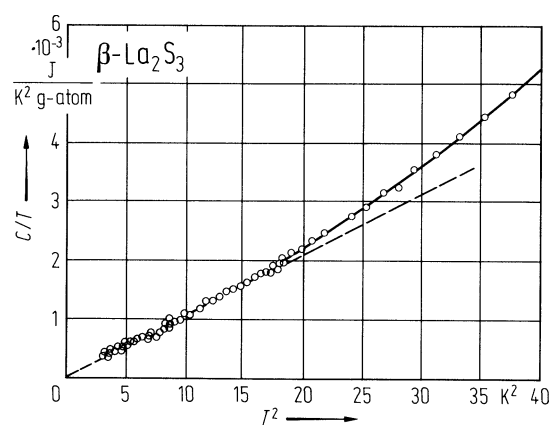
**Fig. 1.**

$\alpha$ -La<sub>2</sub>S<sub>3</sub>. Temperature dependence of heat capacity [81G].



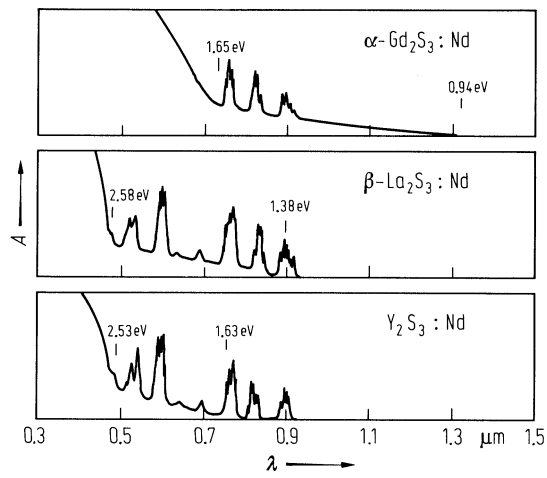
**Fig. 2.**

$\beta$ -La<sub>2</sub>S<sub>3</sub>. Temperature dependence of heat capacity [81G].



**Fig. 3.**

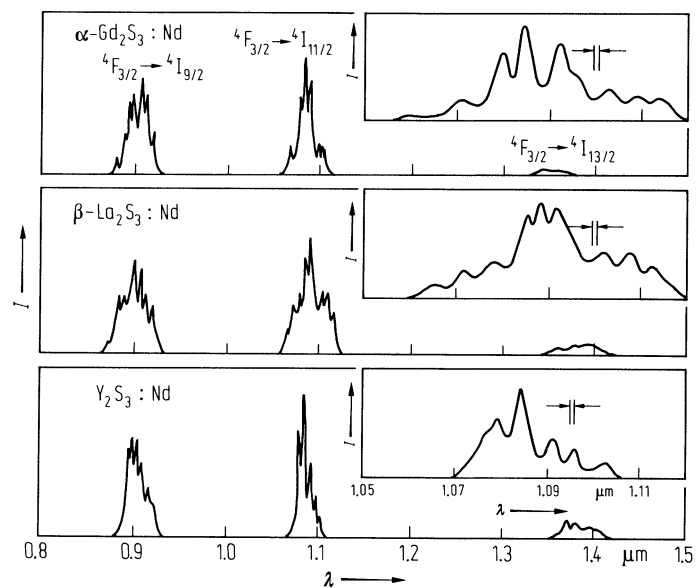
$\alpha$ -Gd<sub>2</sub>S<sub>3</sub>:Nd,  $\beta$ -La<sub>2</sub>S<sub>3</sub>:Nd, Y<sub>2</sub>S<sub>3</sub>:Nd. Absorbance  $A$  vs. wavelength [80L].





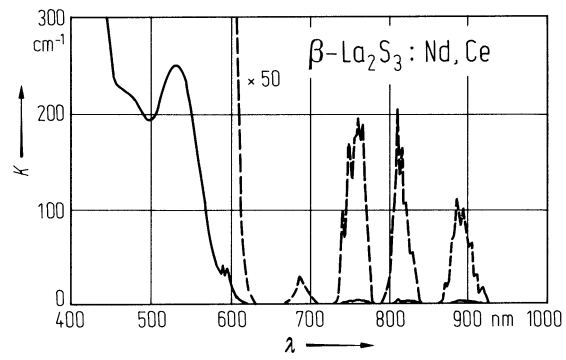
**Fig. 4.**

$\alpha$ -Gd<sub>2</sub>S<sub>3</sub>:Nd,  $\beta$ -La<sub>2</sub>S<sub>3</sub>:Nd, Y<sub>2</sub>S<sub>3</sub>:Nd. Photoluminescence intensity vs. wavelength for  $\alpha$ -Gd<sub>2</sub>S<sub>3</sub>:Nd excited at 752.5 nm,  $\beta$ -La<sub>2</sub>S<sub>3</sub>:Nd and Y<sub>2</sub>S<sub>3</sub>:Nd excited at 600 nm [80L].



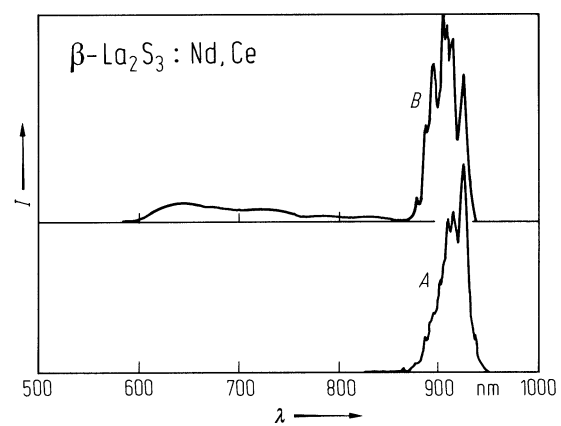
**Fig. 5.**

$\beta$ -La<sub>2</sub>S<sub>3</sub>:Nd,Ce. Absorption spectrum (absorption coefficient vs. wavelength) of Nd(1%) and Ce(1%) co-doped crystals; unpolarized light [82S].



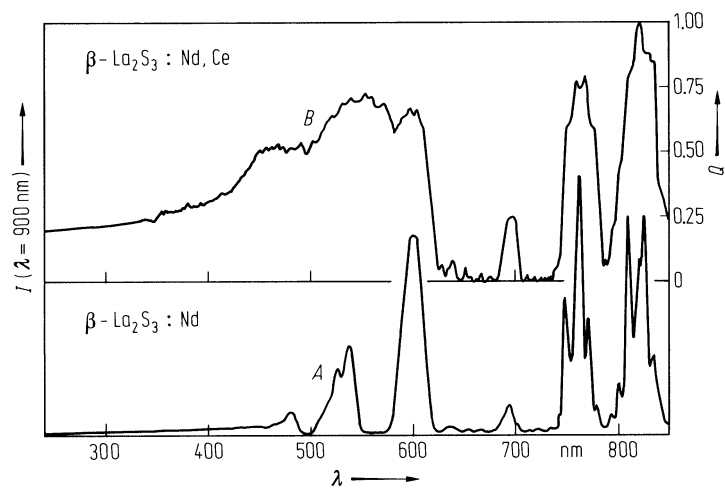
**Fig. 6.**

$\beta$ - $\text{La}_2\text{S}_3$ :Nd,Ce. Fluorescence spectra (fluorescence intensity vs. wavelength) of (A) Nd (10%), Ce(1%) and (B) Nd(1%), Ce (0.2%) codoped crystals [82S].



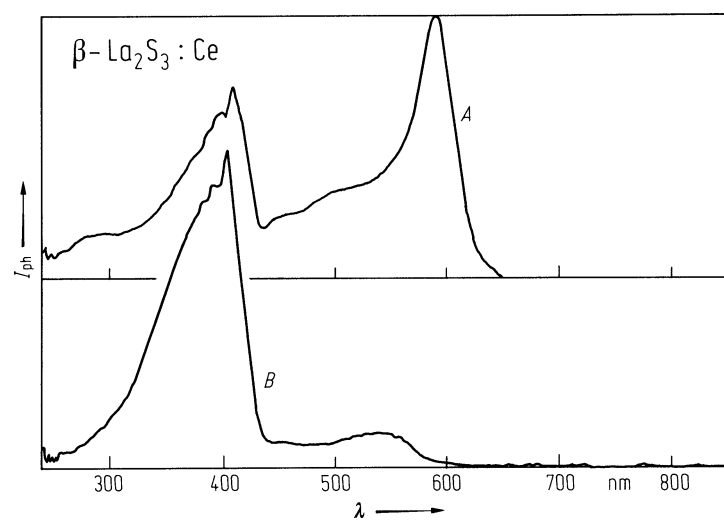
**Fig. 7.**

$\beta\text{-La}_2\text{S}_3\text{:Nd,Ce}$ ;  $\beta\text{-La}_2\text{S}_3\text{:Nd}$ . Excitation spectra of  $\text{Nd}^{3+}$  (fluorescence intensity vs. excitation wavelength) registered at  $\lambda = 900\text{ nm}$  for (A) Nd(1%) and (B) Nd(10%), Ce(1%) doped crystals. The codoped crystal (B) shows efficient energy transfer from band excitation to  $\text{Nd}^{3+}$  [82S].  $Q$ : quantum efficiency of the transfer to  $\text{Nd}^{3+}$ .



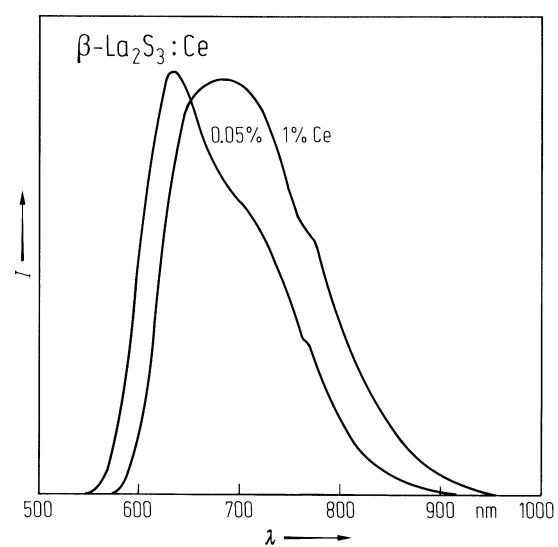
**Fig. 8.**

$\beta$ - $\text{La}_2\text{S}_3$ :Ce. Photoconductivity vs. wavelength for two crystals. (A): 1% Ce, (B): 0.05% Ce doping levels [82S].



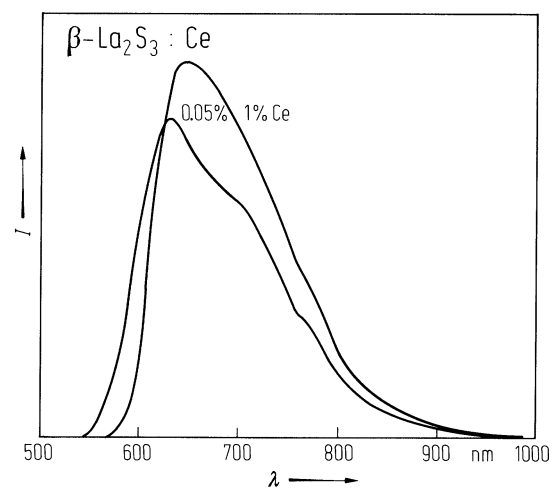
**Fig. 9.**

$\beta$ - $\text{La}_2\text{S}_3$ :Ce. Photoluminescence intensity vs. wavelength for two Ce doping levels [81S]. Excitation wavelength: 540 nm.



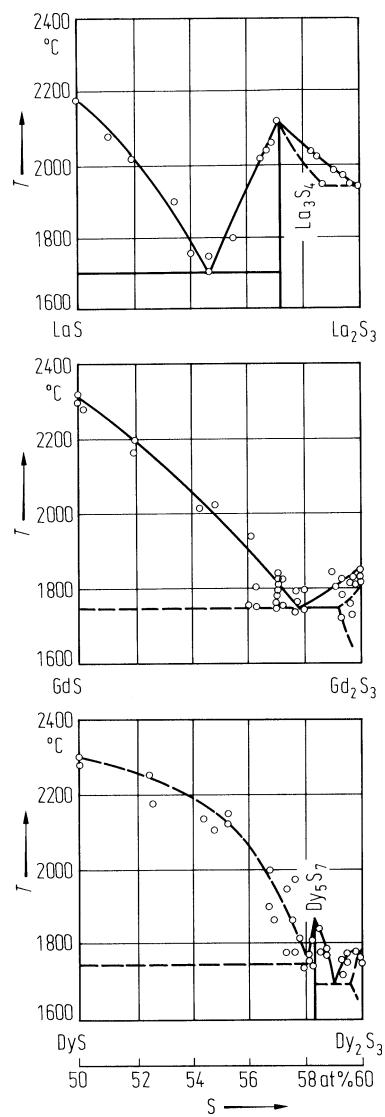
**Fig. 10.**

$\beta$ -La<sub>2</sub>S<sub>3</sub>:Ce. Cathodoluminescence (intensity vs. wavelength) at two Ce doping levels for 20 kV electron beam excitation [81S].



**Fig. 11.**

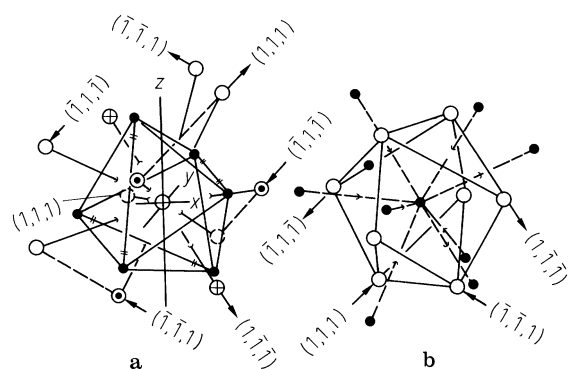
LnS–Ln<sub>2</sub>S<sub>3</sub> system, Ln = La, Gd, Dy. Phase diagrams [81K].





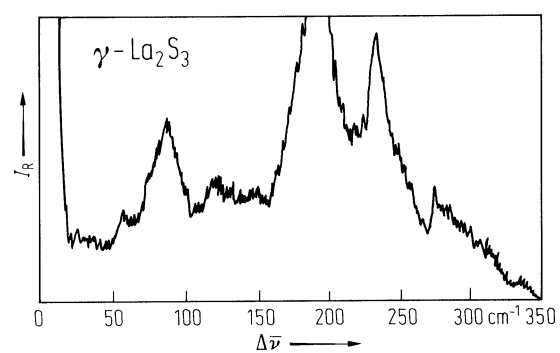
**Fig. 12.**

Th<sub>3</sub>P<sub>4</sub>-type compounds. The coordination polyhedra of the cations and the anions. Full circles: Th- atoms, other circles: P-atoms [66H].



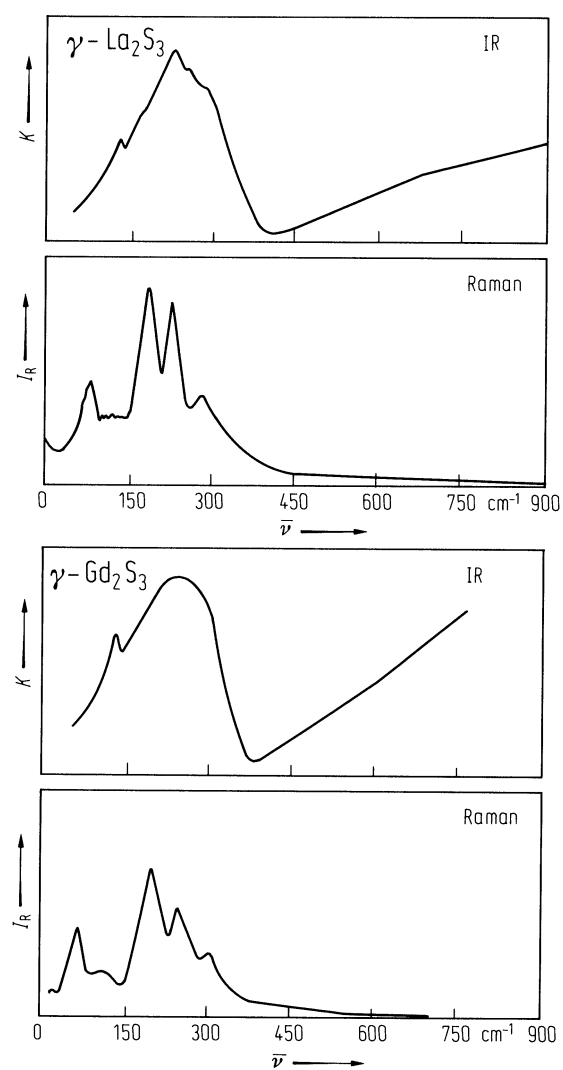
**Fig. 13.**

$\gamma$ -La<sub>2</sub>S<sub>3</sub>. Raman intensity vs. Raman shift (in wavenumbers) [79A].



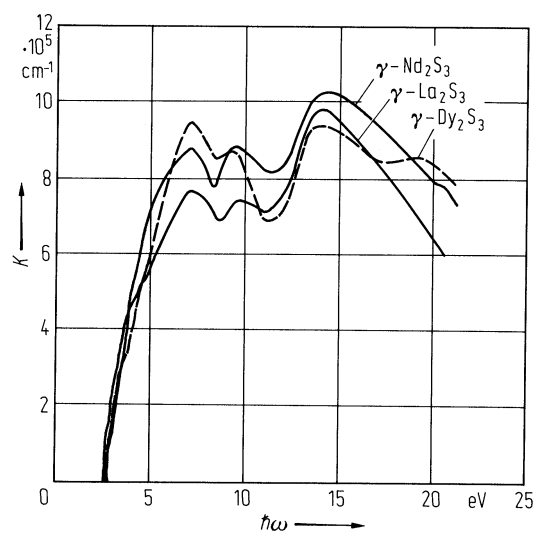
**Fig. 14.**

$\gamma$ - $\text{La}_2\text{S}_3$ ,  $\gamma$ - $\text{Gd}_2\text{S}_3$ . Infrared absorption and Raman intensity vs. wavenumber at 300 K [67B].



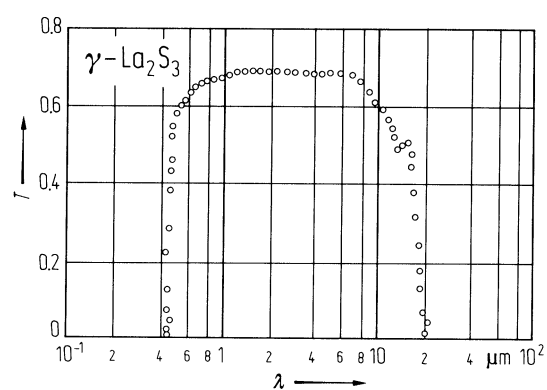
**Fig. 15.**

$\gamma$ - $\text{La}_2\text{S}_3$ ,  $\gamma$ - $\text{Nd}_2\text{S}_3$ ,  $\gamma$ - $\text{Dy}_2\text{S}_3$ . Absorption coefficient vs. photon energy [79Z].



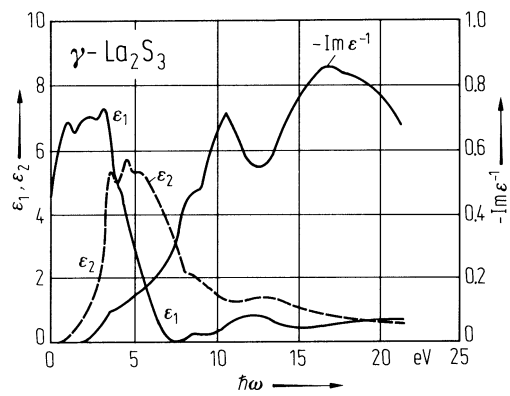
**Fig. 16.**

$\gamma$ -La<sub>2</sub>S<sub>3</sub>. Transmission spectrum (transmission vs. wavelength) of a 315  $\mu\text{m}$  thick single crystal platelet [81K].



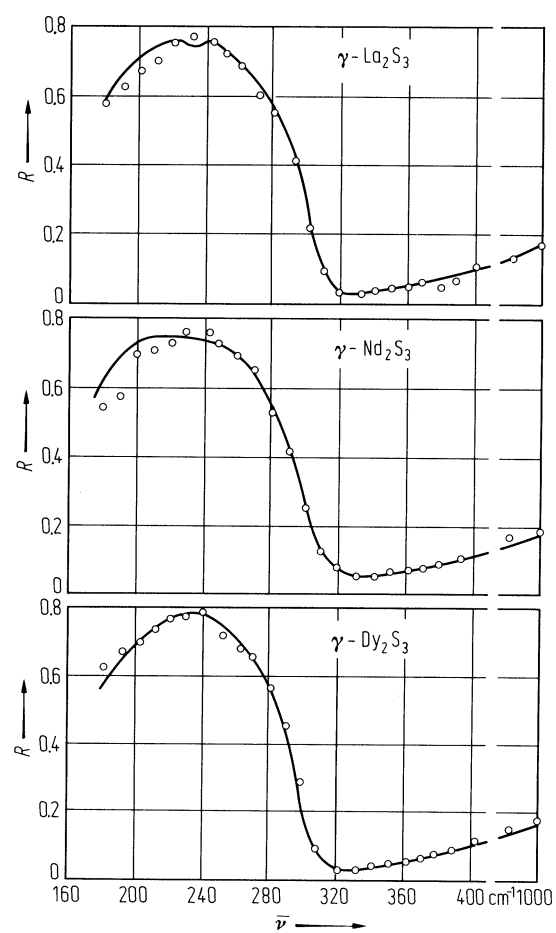
**Fig. 17.**

$\gamma$ - $\text{La}_2\text{S}_3$ . Real and imaginary parts of the dielectric constant and energy loss function vs. photon energy [79Z].



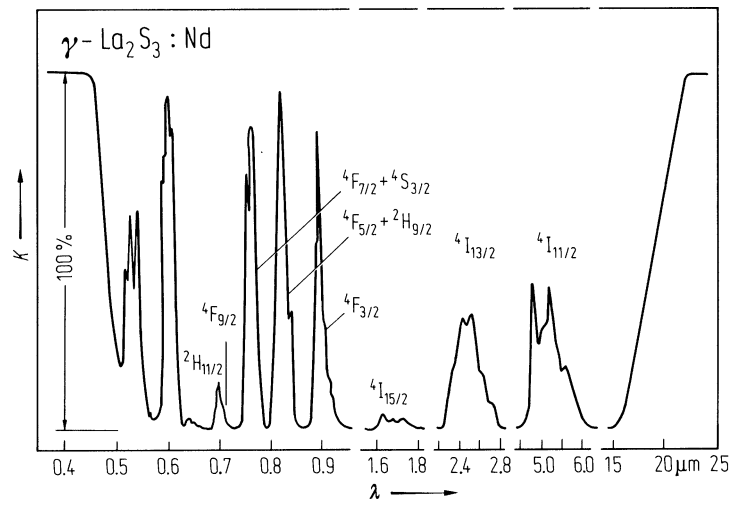
**Fig. 18.**

$\gamma$ - $\text{La}_2\text{S}_3$ ,  $\gamma$ - $\text{Nd}_2\text{S}_3$ ,  $\gamma$ - $\text{Dy}_2\text{S}_3$ . Reflectivity vs. wavenumber in the infrared range [79A].



**Fig. 19.**

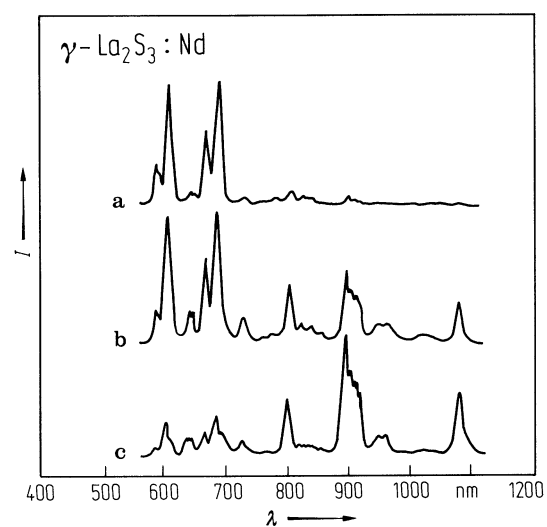
$\gamma$ - $\text{La}_2\text{S}_3:\text{Nd}$ . Absorption coefficient vs. wavelength at 300 K [80K]. Cf. Figs. 21, 22.





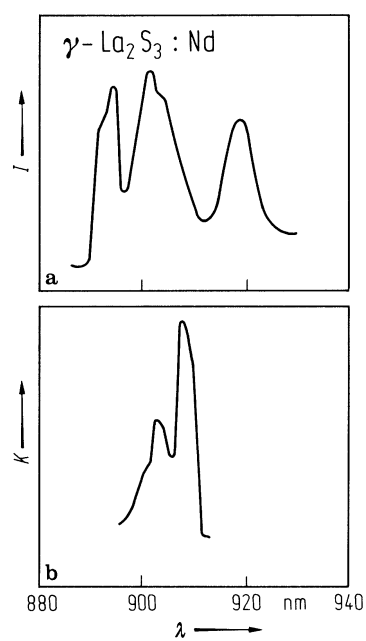
**Fig. 20.**

$\gamma$ - $\text{La}_2\text{S}_3:\text{Nd}$  (0.9%). Luminescence spectra (intensity vs. wavelength) with 530 nm excitation taken 1  $\mu\text{s}$  (a), 5  $\mu\text{s}$  (b), and 10  $\mu\text{s}$  (c) after excitation [83K2].



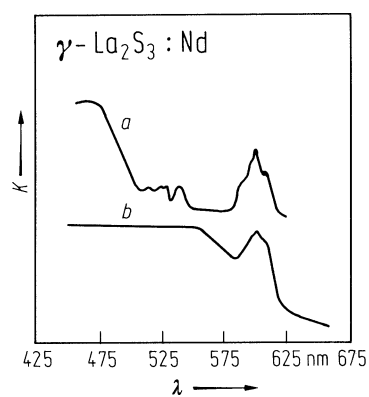
**Fig. 21.**

$\gamma$ - $\text{La}_2\text{S}_3:\text{Nd}$  (0.9%). Luminescence intensity (a) and absorption coefficient (b) vs. wavelength at 4.2 K [83K2].



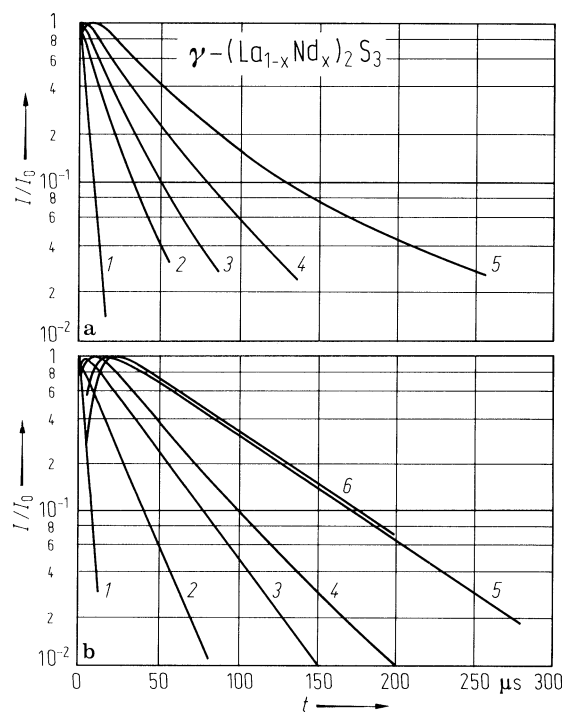
**Fig. 22.**

$\gamma$ - $\text{La}_2\text{S}_3$  Nd (0.9%). Absorption coefficient vs. wavelength at 300 K (a) and 600 K (b) [83K1]. Cf Fig. 19.



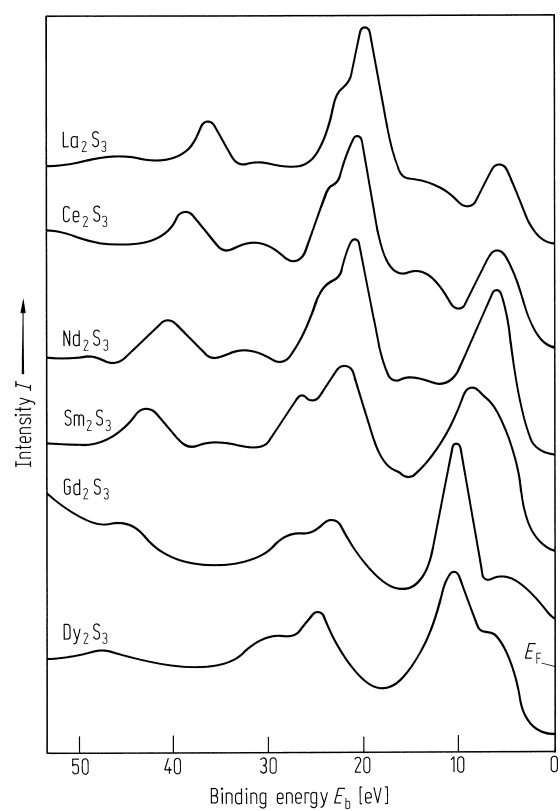
**Fig. 23.**

$\gamma-(\text{La}_{1-x}\text{Nd}_x)_2\text{S}_3$ . Temporal evolution of the  $^4\text{F}_{3/2}$  neodymium population for  $x = 0.27$  (1), 0.073 (2), 0.046 (3), 0.027 (4), 0.009 (5), and 0.003 (6) after a short pulse excitation at 530 nm (a) and 600 nm (b). (Normalized fluorescence intensity  $I/I_0$  vs. time  $t$ ) [83K2].



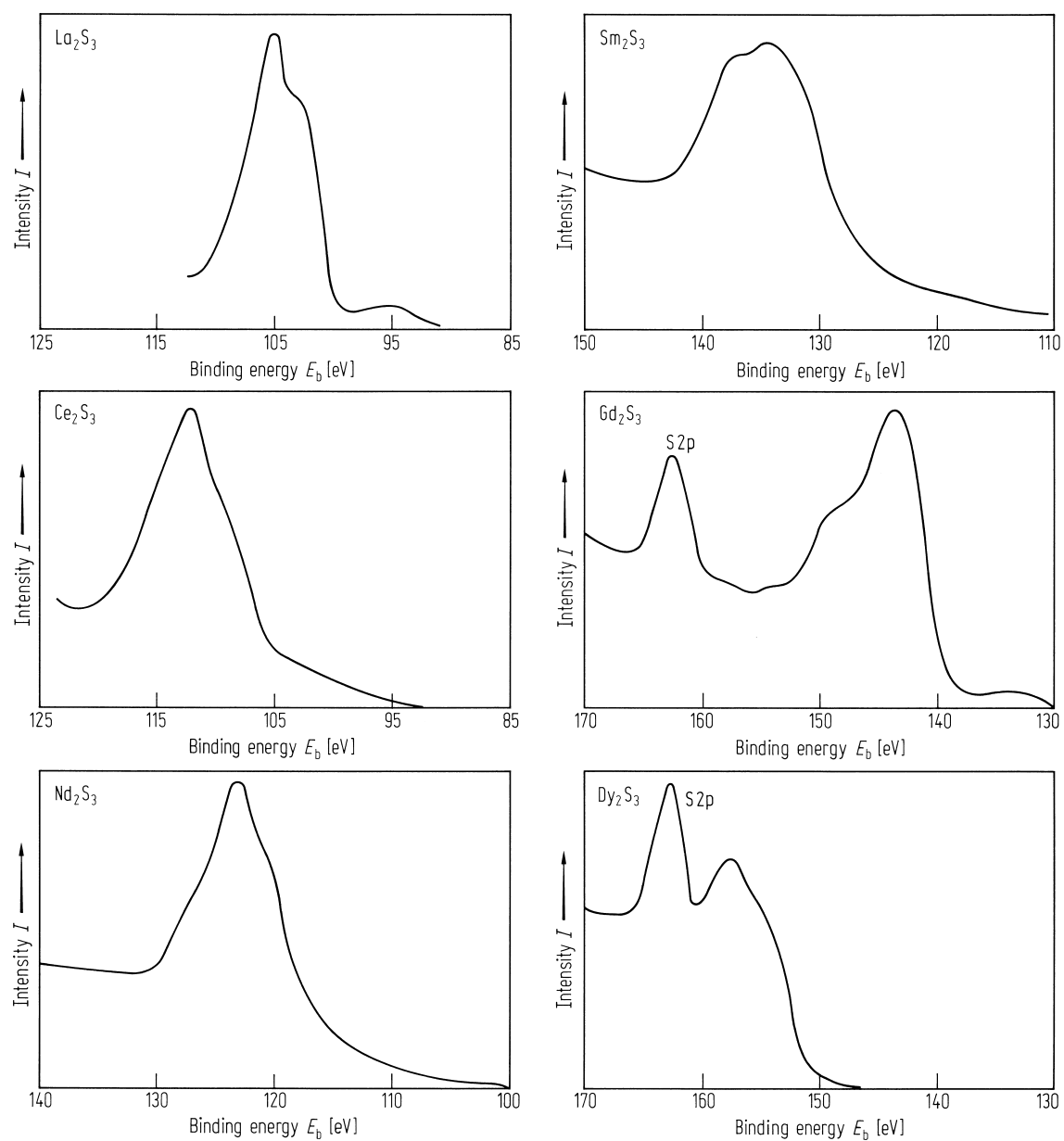
**Fig. 24.**

$\gamma$ - $\text{Ln}_2\text{S}_3$ .  $\text{MgK}\alpha$  X-ray photoelectron spectra of the rare-earth sesquisulfides ( $\text{Ln} = \text{La, Ce, Nd, Sm, Gd, Dy}$ ) in the energy region below Fermi level down to Ln 5s core level [91K].



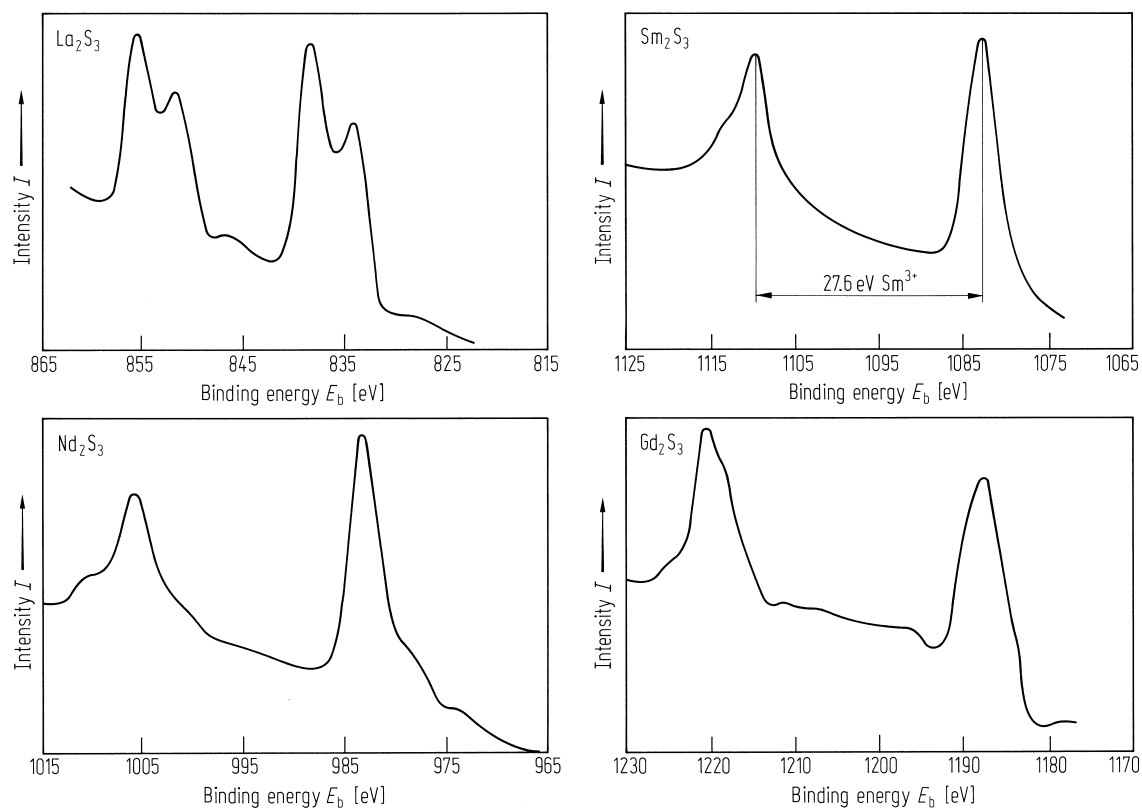
**Fig. 25.**

$\gamma$ - $\text{Ln}_2\text{S}_3$ .  $\text{MgK}_{\alpha}$  X-ray photoelectron spectra of the rare-earth sesquisulfides ( $\text{Ln} = \text{La, Ce, Nd, Sm, Gd, Dy}$ ) in the 4d core level region [91K].  $E_b$  relative to  $E_F$ .



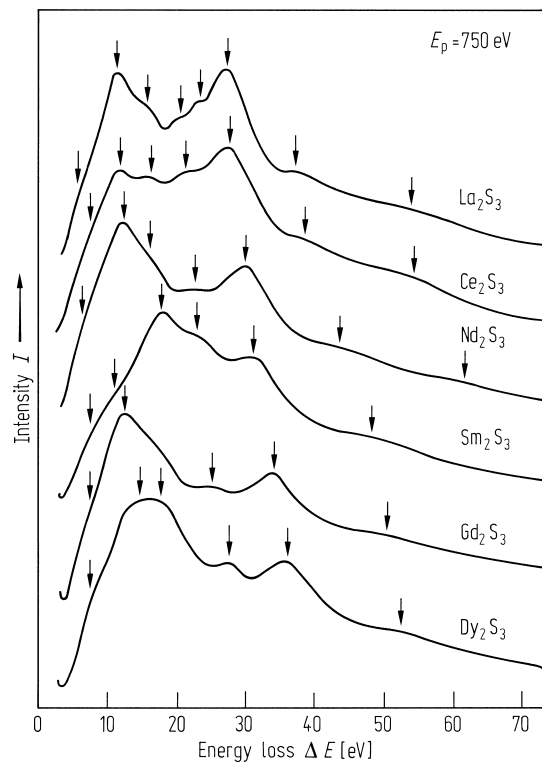
**Fig. 26.**

$\gamma$ - $\text{Ln}_2\text{S}_3$ .  $\text{AlK}_\alpha$  X-ray photoelectron spectra of the rare-earth sesquisulfides ( $\text{Ln} = \text{La, Nd, Sm, Gd}$ ) in the 3d core level region [91K]. The trivalence of Sm is testified by the value of the Sm 3d doublet line spin-orbit splitting ( $= 27.6 \text{ eV}$ ).  $E_b$  relative to  $E_F$ .



**Fig. 27.**

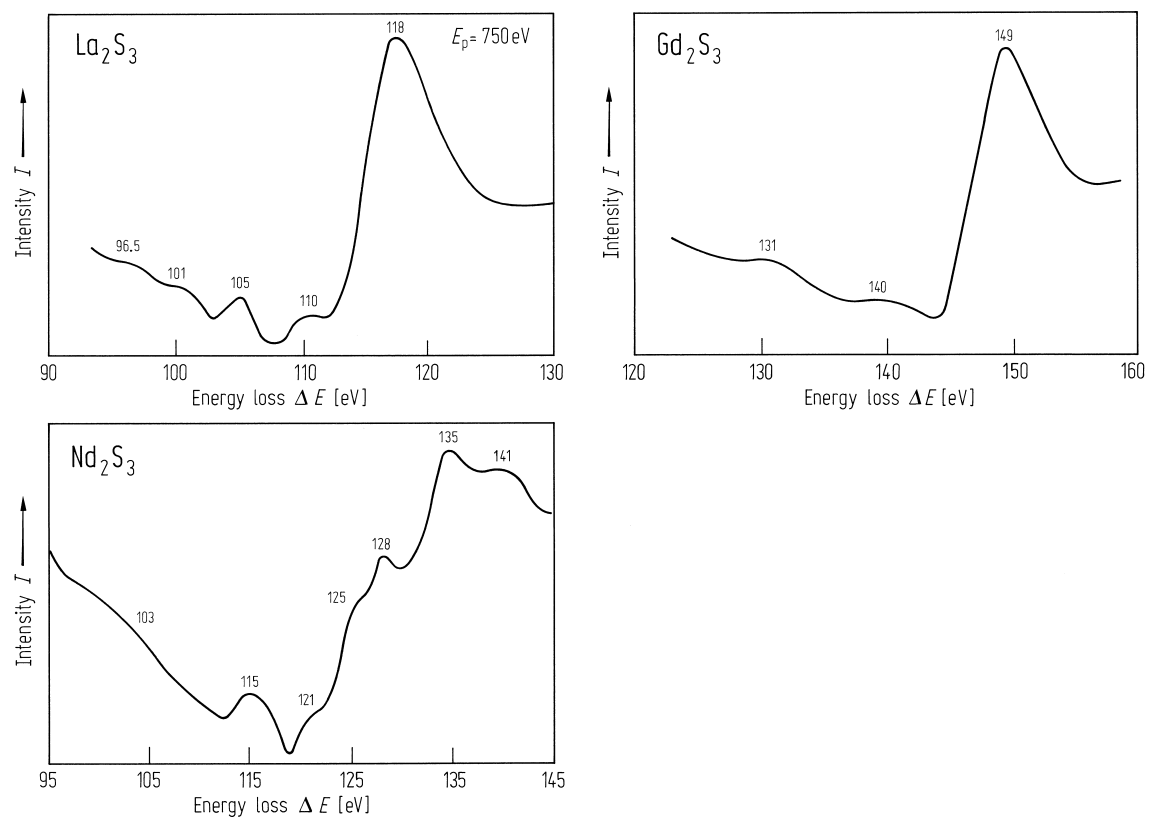
$\gamma$ - $\text{Ln}_2\text{S}_3$ . Electron loss spectra of the rare-earth sesquisulfides ( $\text{Ln} = \text{La, Ce, Nd, Sm, Gd, Dy}$ ) for primary electron beam energy  $E_p = 750 \text{ eV}$ . All the peaks, revealed from the second derivative  $d^2N/dE^2$  are indicated by arrows [91K].





**Fig. 28.**

$\gamma$ - $\text{Ln}_2\text{S}_3$ ,  $\text{Ln} = \text{La, Nd, Gd}$ . 4f-4f giant resonance in energy loss spectra at primary electron energy  $E_p = 750$  eV after Shirley background subtraction [91K].



**Fig. 29.**

$\gamma$ - $\text{La}_2\text{S}_3$ ;  $\gamma$ - $\text{Sm}_2\text{S}_3$ . Reflection spectra [83B].

