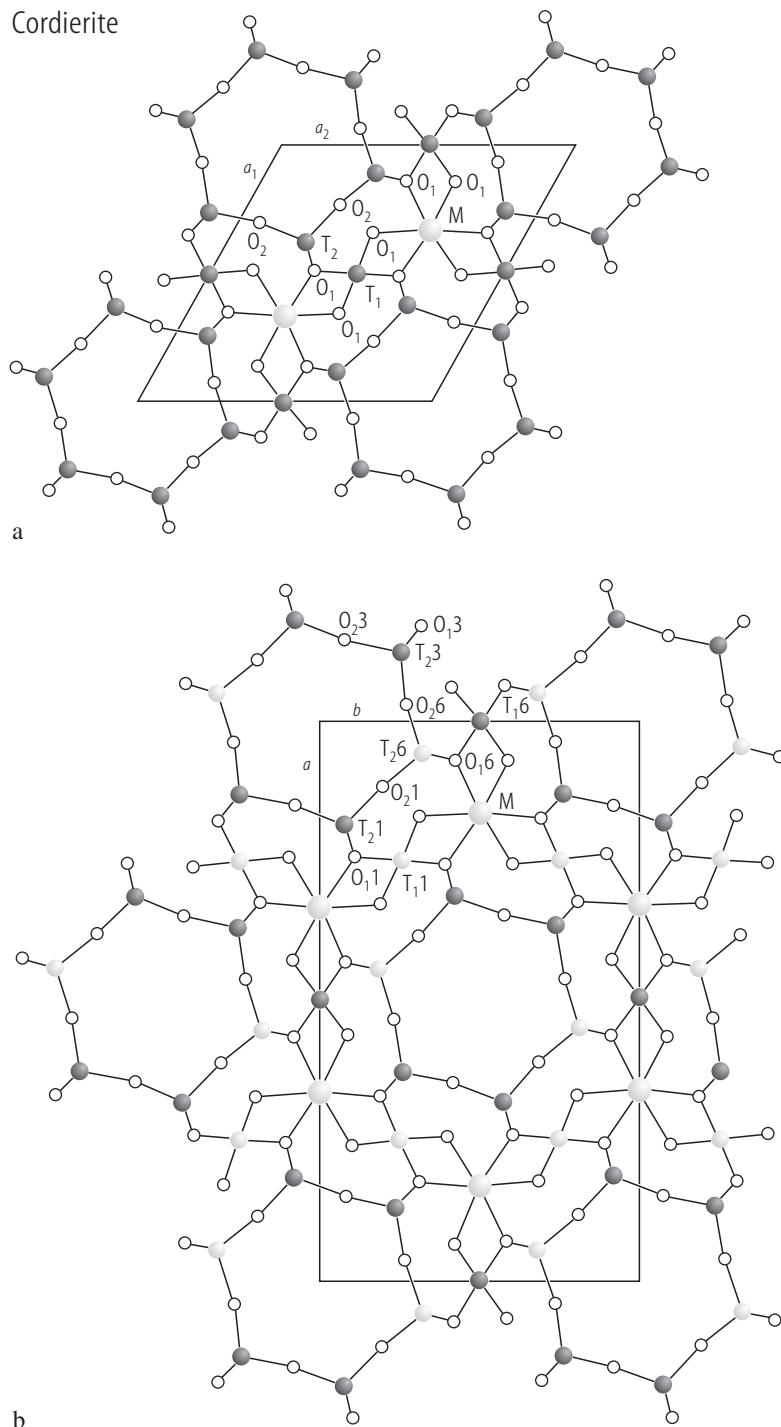
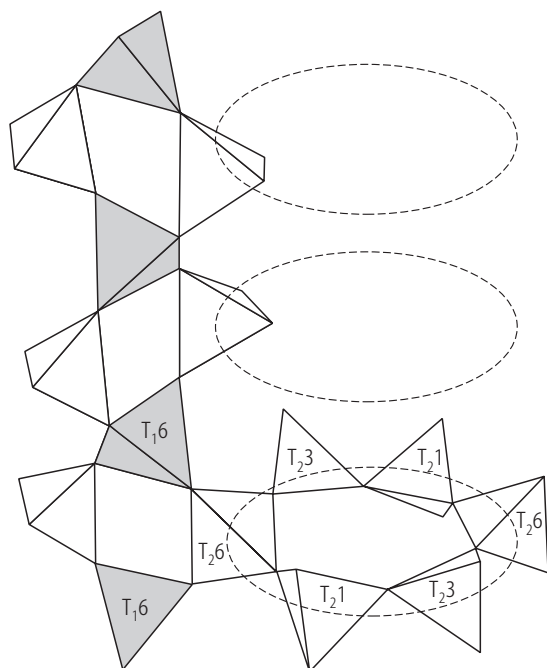


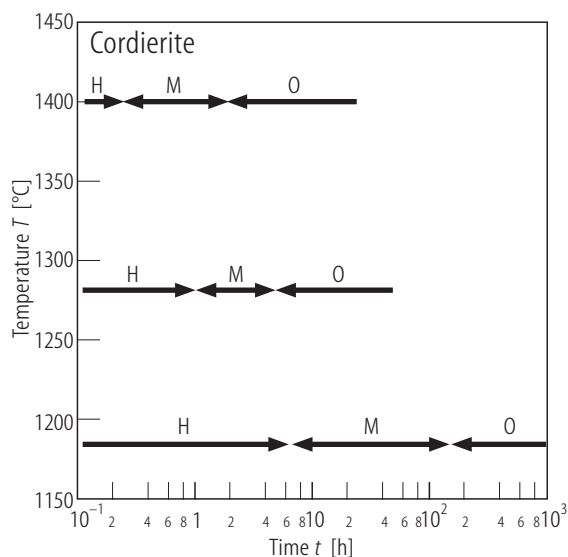
## Cordierite



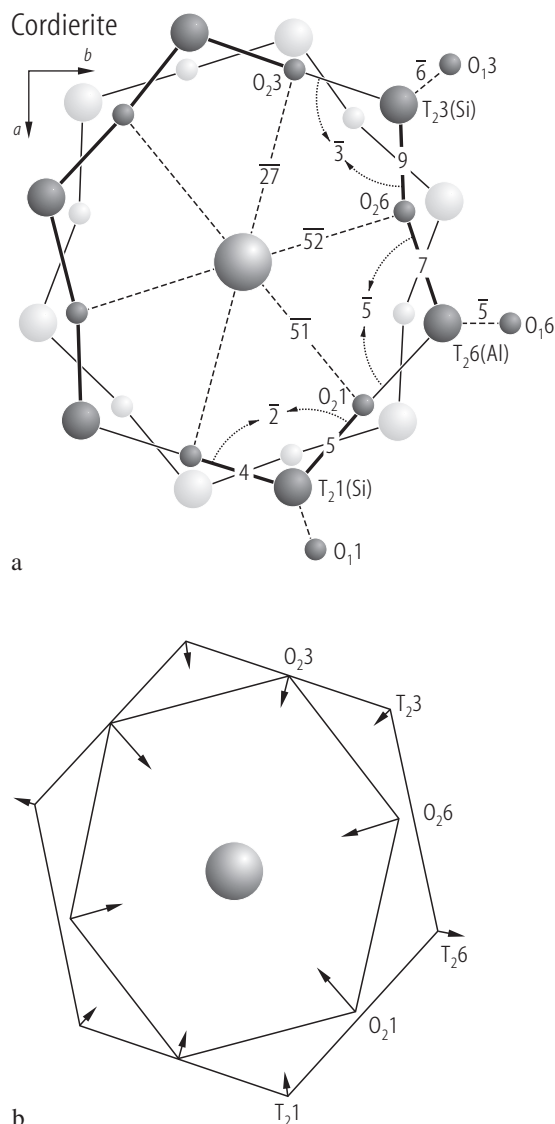
**Fig. 1.** Cordierites. *c*-axis projection of (a) hexagonal form and (b) idealized orthorhombic form. In hexagonal structure  $T_1$  sites are Si-rich and  $T_2$  are Al-rich. In the orthorhombic low cordierite structure, full  $T_1$ ,  $T_2$  circles are Si and open  $T_1$ ,  $T_2$  circles are Al [77M1].

$\beta$ -Cordierite

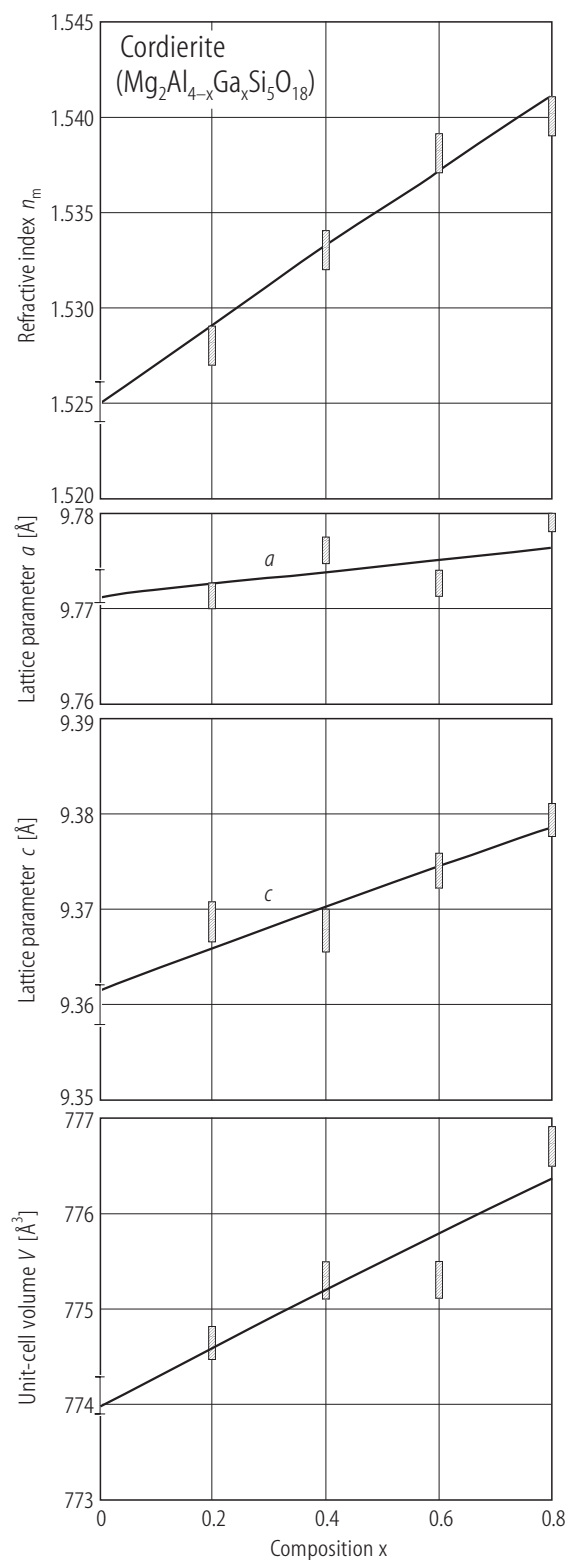
**Fig. 2.**  $\beta$ -Cordierite. The arrangement of tetrahedra. Each  $T_2$  tetrahedron in the rings is joined via a  $T_1$  tetrahedron (shaded) to the ring above and the ring below, such that all tetrahedra are corner sharing. The dashed lines show the position of similar rings of  $T_2$  tetrahedra forming channels, only one of which is shown along the  $c$ -axis [85P1].



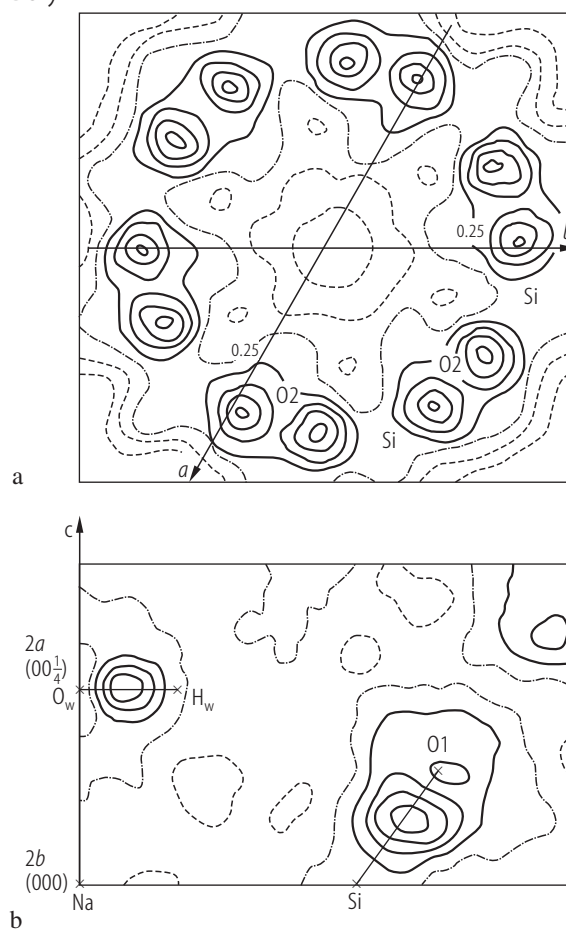
**Fig. 4.** Cordierites. Time-temperature diagram for the formation of three different cordierite phases by dry annealing cordierite glass [87P2] (H – hexagonal, M – modulated, O – orthorhombic).



**Fig. 3.** Low cordierite. Distortion of the six-membered rings of tetrahedra owing to Na incorporation. **(a)** Ring at  $z = 0$  is emphasized by connection of dark shaded circles centered by Na at Ch0 (site symmetry 222). Light shaded circles indicate atom positions at  $z = \pm 1/2$ . Decrease of Ch0–O distances owing to Na in Ch0 is indicated by dashed lines. The amount of change is given in 0.001 Å. Heavy solid lines specify increased anion-cation distances. Decrease of T–O–T angles is shown by dotted curves given for each angle. The change of angles is in full degrees. **(b)** Oxygen atoms at  $z = 0$  are connected with each other to form an inner ring. Also shown are cations at  $z = 0$  to form an outer ring. Arrows indicate the relative motion due to Na incorporation. The oxygen ring contracts mainly along the vector Na– $T_{26}$ , whereas the cation ring expands along this direction [86A2].



Beryl



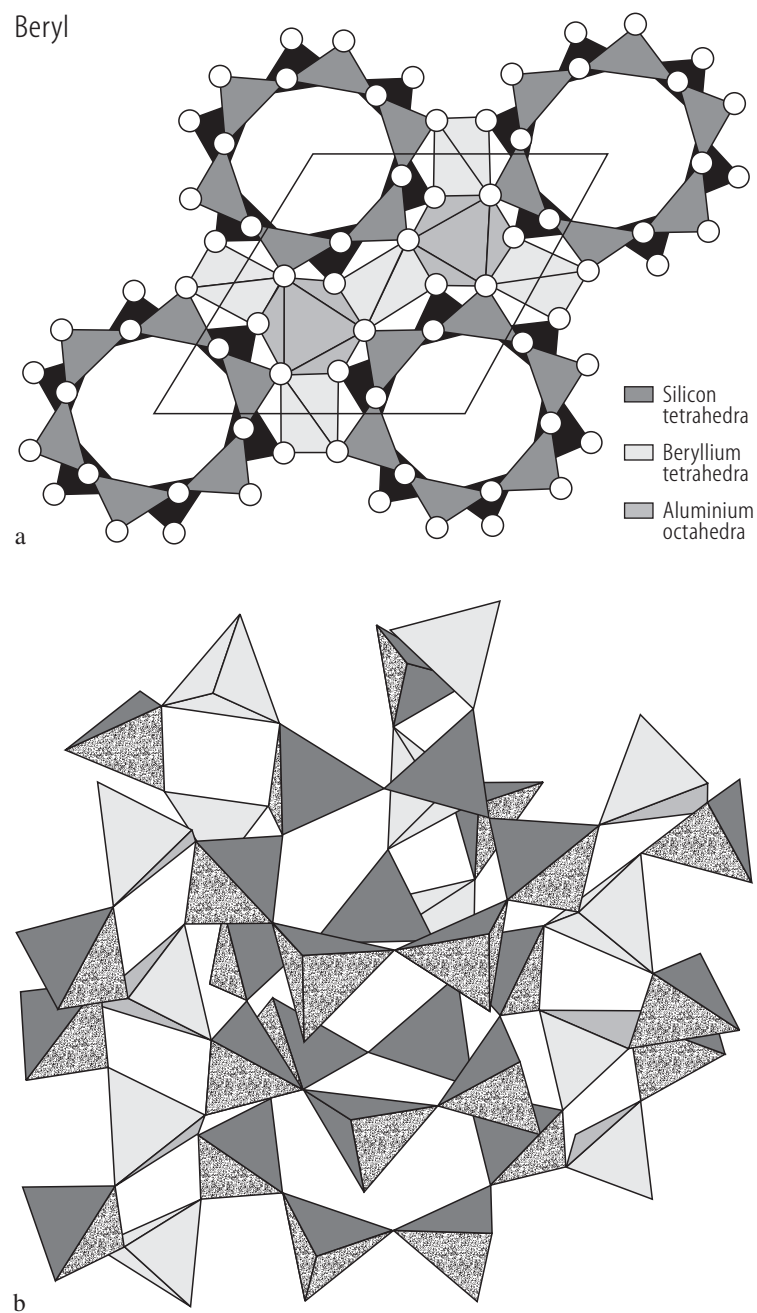
**Fig. 7.** Beryl<sup>40</sup>. (a)  $\delta\rho$  map through  $[\text{Si}_6\text{O}_{18}]^{12-}$  ring. (b)  $\delta\rho$  map through hexagonal channel and O1–O1 edge of  $\text{SiO}_4$  tetrahedron [88E1]. Contours spacing  $0.1 \text{ e}\text{\AA}^{-3}$ .

For Fig. 6 see next page

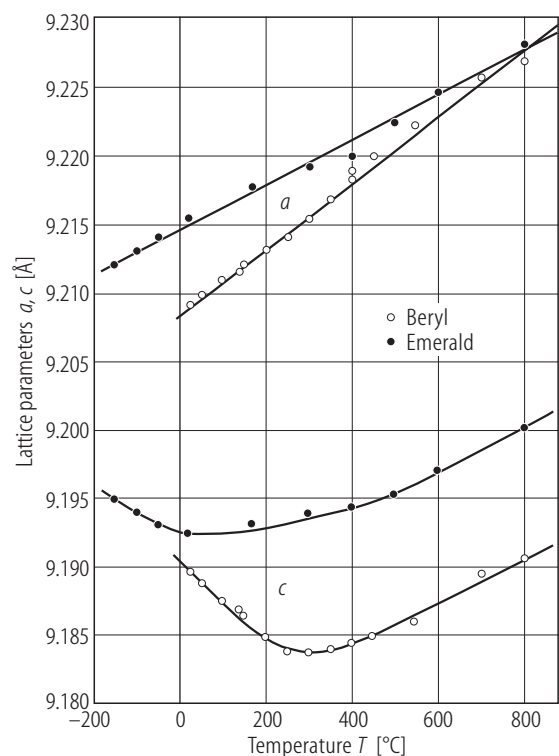
←

**Fig. 5.** Ga-bearing cordierites. Lattice parameters and unit cell volume as function of composition [71L1]. The samples were obtained through devitrification of glasses at 1 atm and  $1050^\circ\text{C}/110 \text{ h}$ . The refractive index is also given.

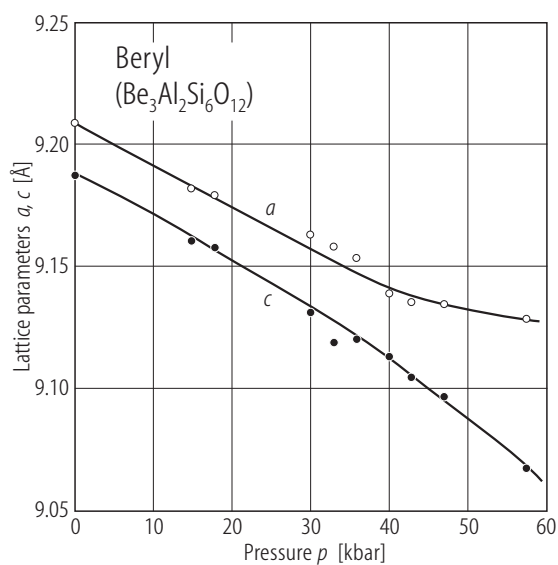
## Beryl



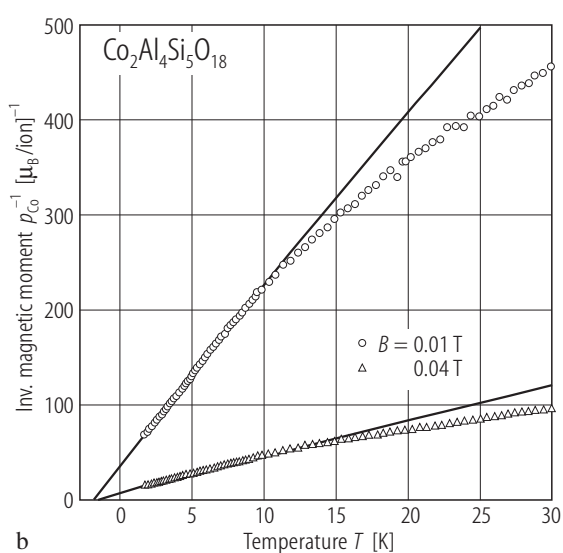
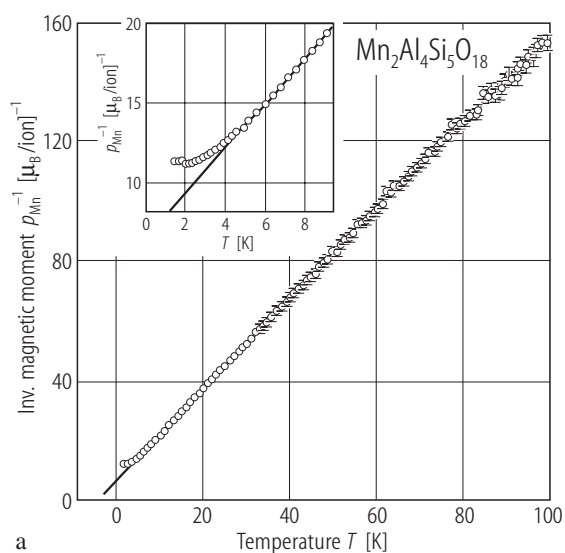
**Fig. 6.** Beryl. Crystal structure [68G1]. **(a)** The *c*-axis projection shows the six-membered tetrahedral rings of Si, which are cross-linked by Be tetrahedra and Al octahedra. **(b)** The arrangement of Si and Be tetrahedra resulting in a continuous three-dimensional framework.



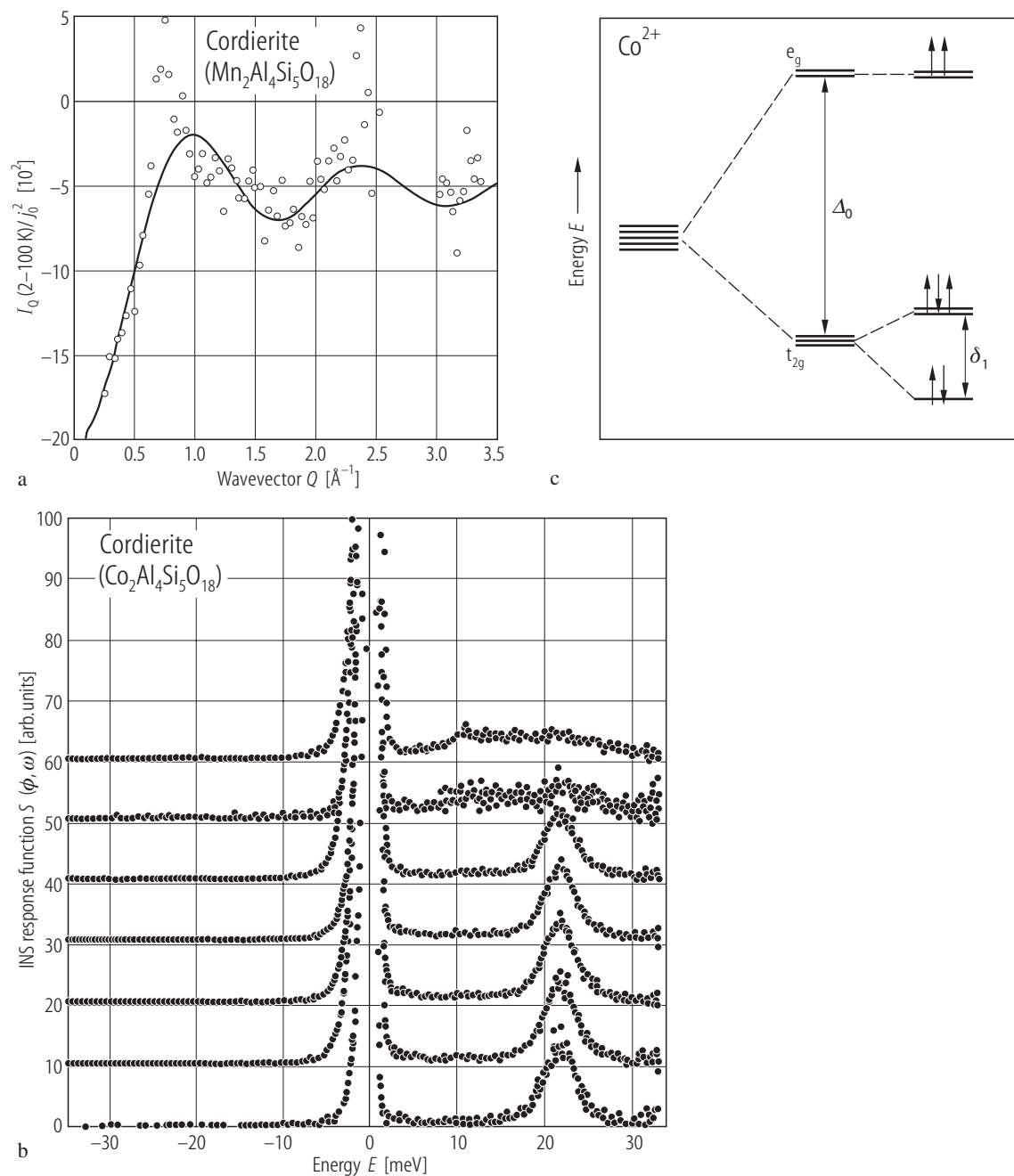
**Fig. 8.** Beryl<sup>[36]</sup> (o) and emerald<sup>[41]</sup> (•). Temperature dependences of the lattice parameters [72M1]. Smooth curves have been drawn through the points for the *c*-axes and straight lines were drawn through the points for the *a*-axes.



**Fig. 9.** Beryl<sup>[42]</sup>. Pressure dependences of lattice parameters [86H1].



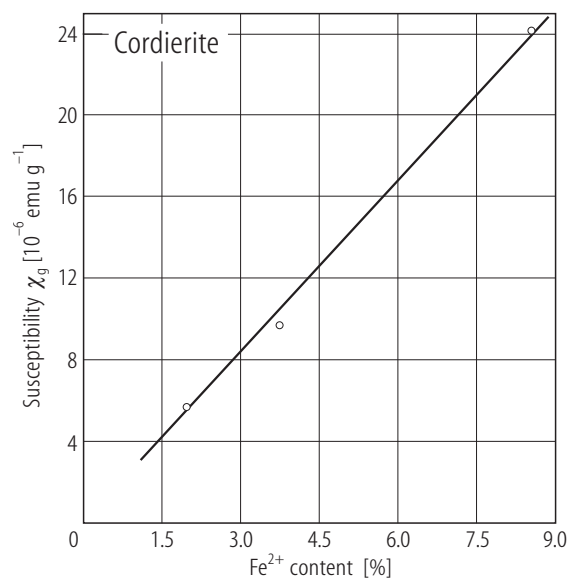
**Fig. 10.**  $\text{Mn}_2\text{Al}_4\text{Si}_5\text{O}_{18}$  (a),  $\text{Co}_2\text{Al}_4\text{Si}_5\text{O}_{18}$  (b) cordierites. Temperature dependences of the inverse magnetic moments [99K1]. The solid lines in (b) correspond to the fit of the paramagnetic Curie-Weiss law for  $T < 10$  K.



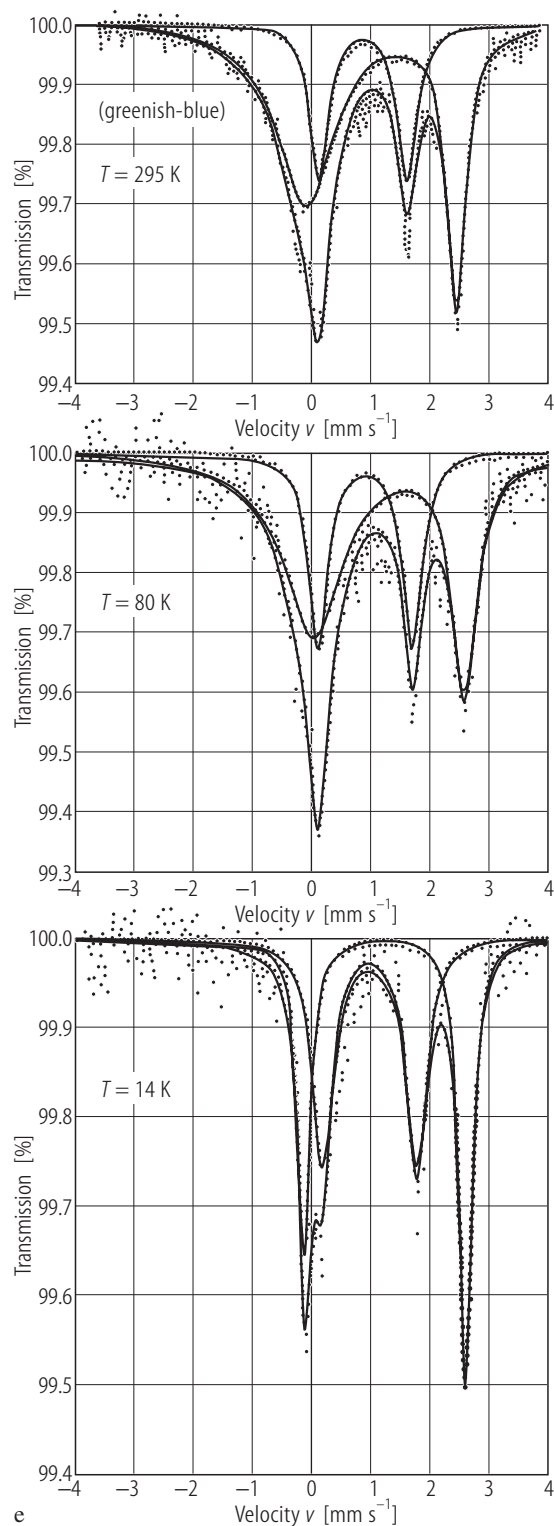
**Fig. 12.**  $\text{Mn}_2\text{Al}_4\text{Si}_5\text{O}_{18}$  cordierite (a). Fit of a Blech-Averbach function for  $\text{Mn}^{2+}$  nearest neighbour interaction through the normalized difference signal  $I_Q(2-100)/j_0^2$ .  $I_Q/j_0^2$  is the magnetic scattering intensity as function of the scattering vector  $Q = 2\pi \sin \theta / \lambda$  normalized by the magnetic

form factor  $j_0$  [99K1]. –  $\text{Co}_2\text{Al}_4\text{Si}_5\text{O}_{18}$  cordierite (b). Magnetic scattering [97W1]. (c) The splitting of the 3d-orbitals. The relative energy levels due to octahedral coordination (center) and the splitting for a trigonal distortion (right hand side) are given [93B1, 97W1].

For Fig. 11 see next page



**Fig. 11.** Cordierites. Magnetic susceptibilities versus  $\text{Fe}^{2+}$  content [68P1].



**Fig. 13e.**

**Fig. 13.** Beryls.  $^{57}\text{Fe}$  NGR spectra. Deep blue beryl at (a) 4.2, 30 and 295 K (type I fit) and (b) type II fit at 4.2 and 295 K; (c) light blue beryl at 14 and 295 K; (d) bluish green beryl at 80 and 295 K; (e) greenish blue beryl at 14, 80 and 295 K [02V1].

For Figs. 13a, b, c, d see next pages

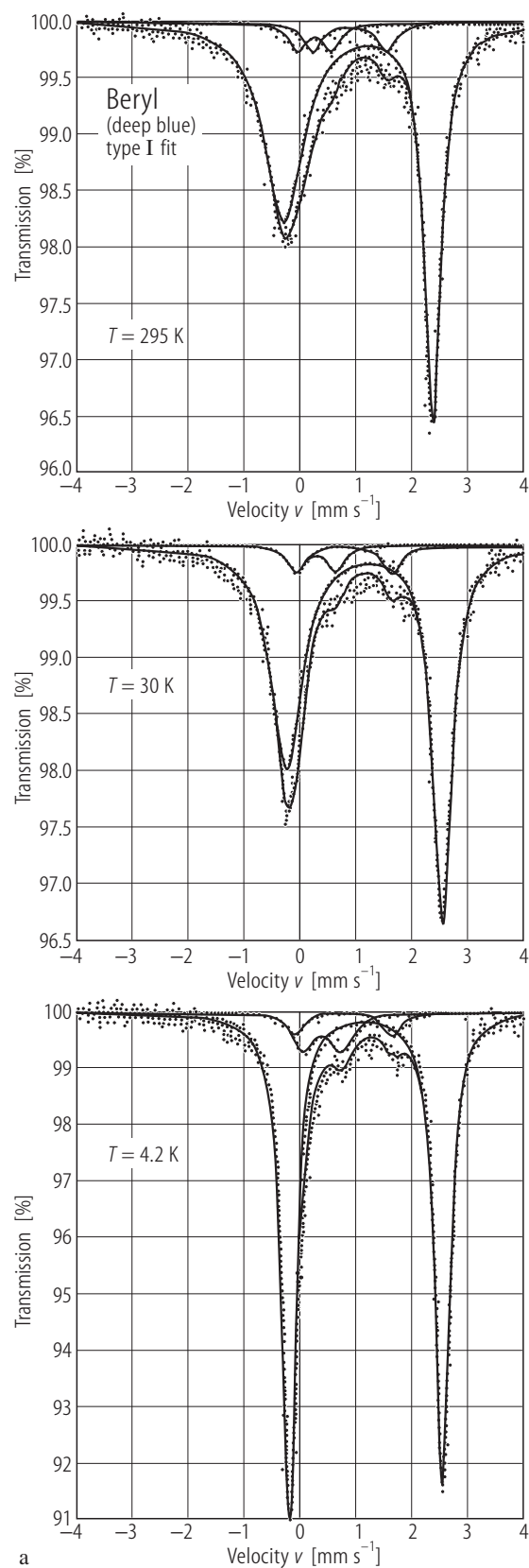
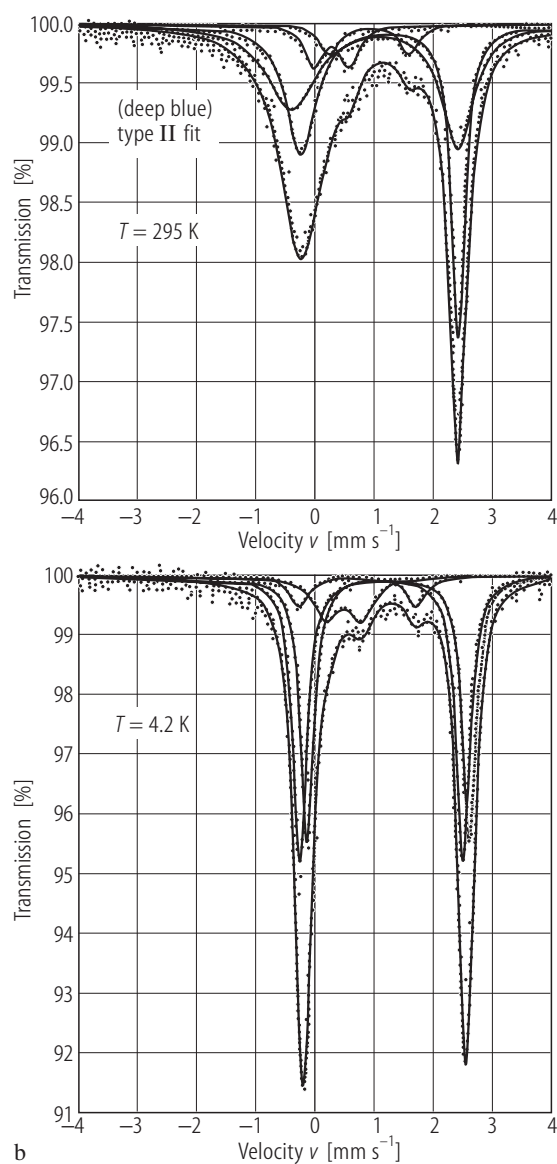
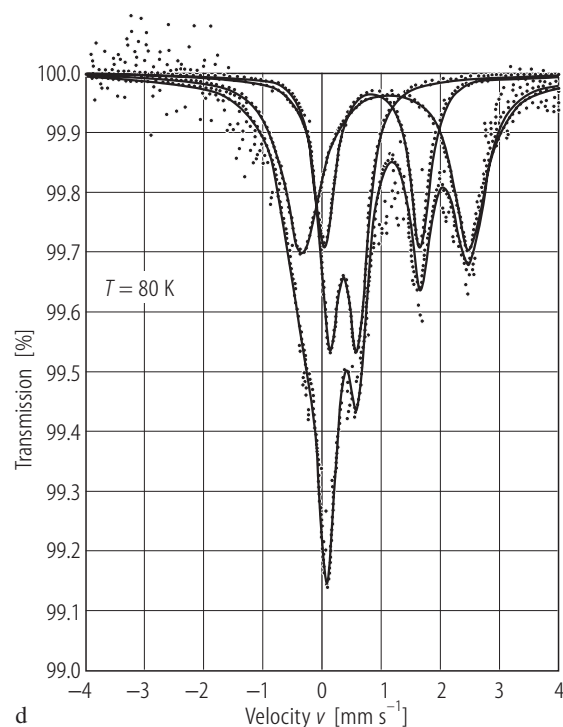
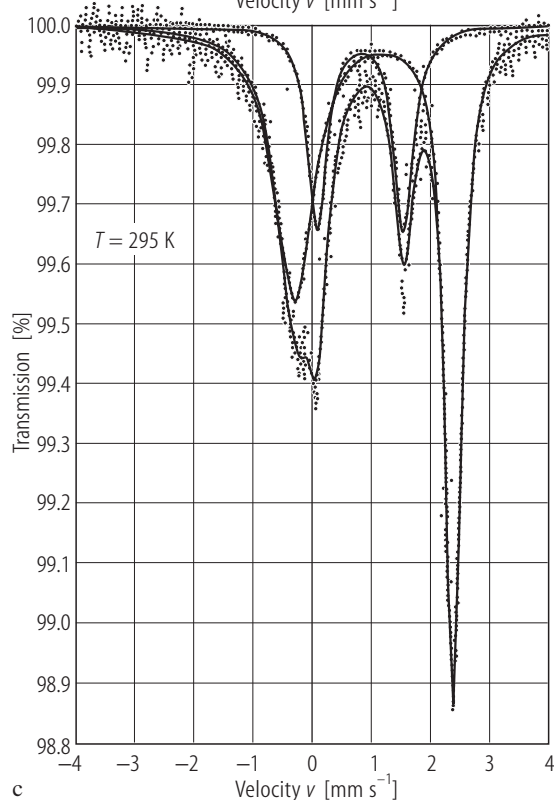
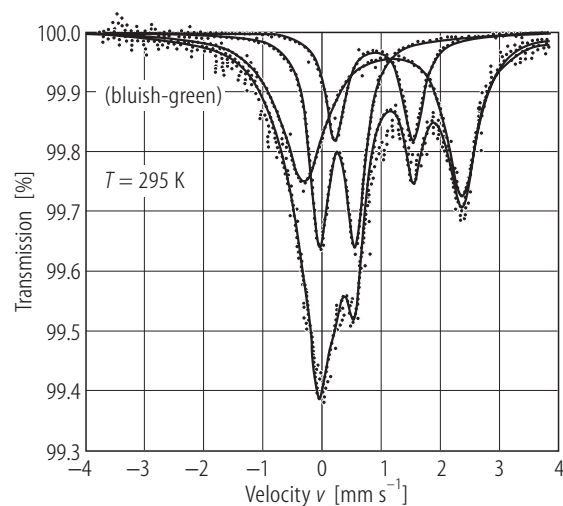
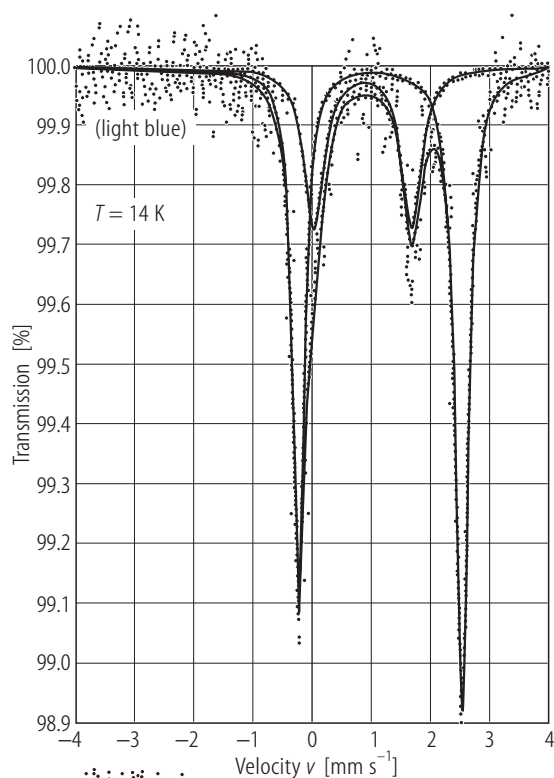


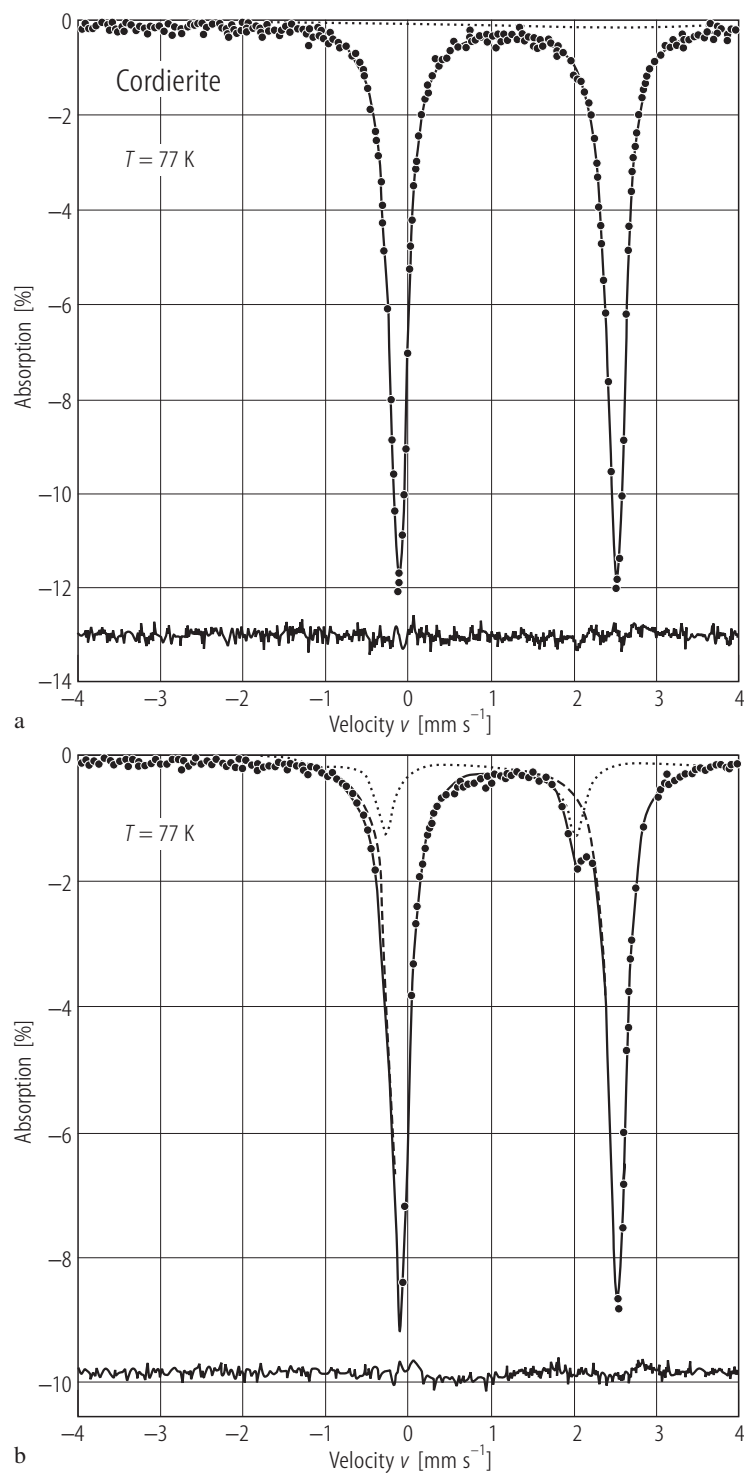
Fig. 13 a, b. For caption see previous page



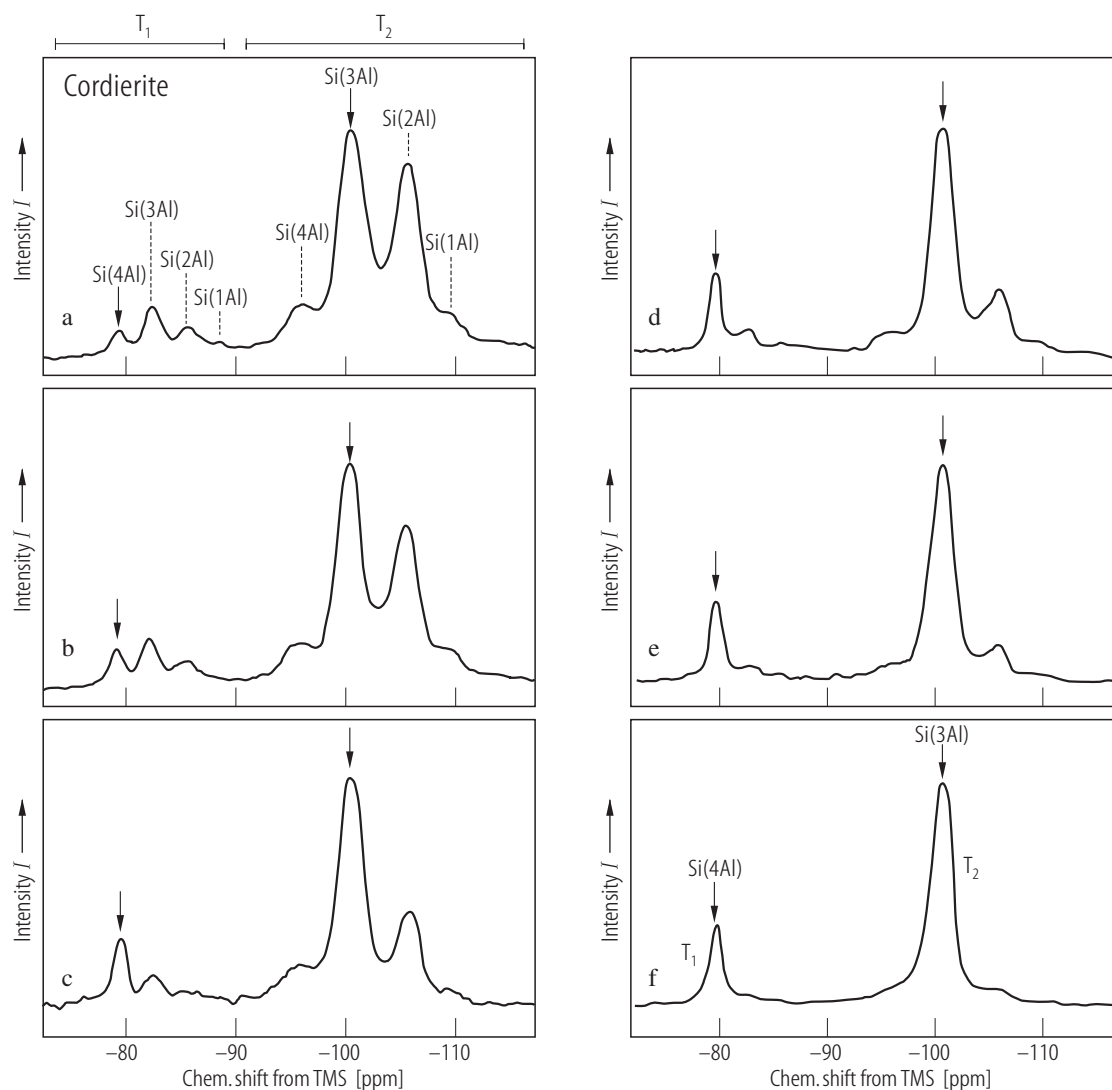




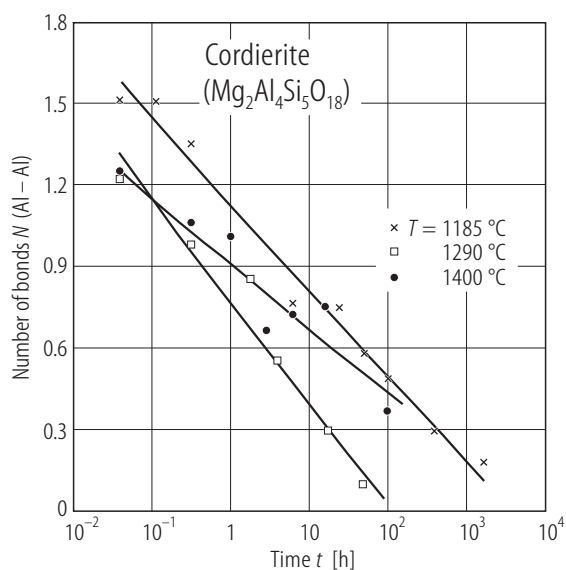
**Fig. 13c, d.** For caption see p. 104.



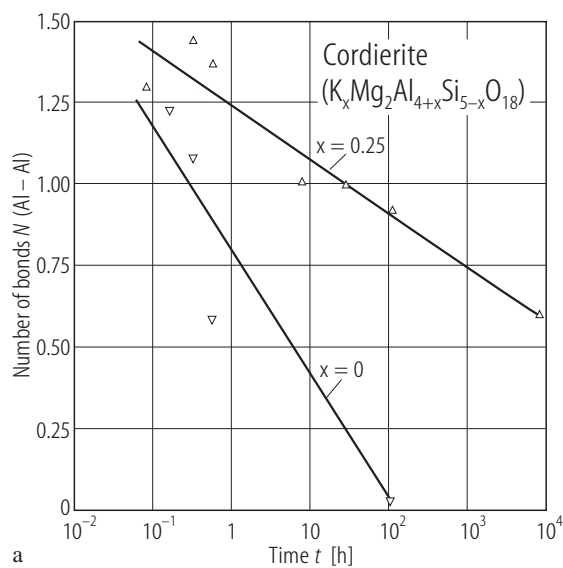
**Fig. 14.** Cordierite.  $^{57}\text{Fe}$  NGR spectra at 77 K: (a) natural sample<sup>33</sup>, (b) natural sample<sup>32</sup> (compositions according to Table 3) [00G1].



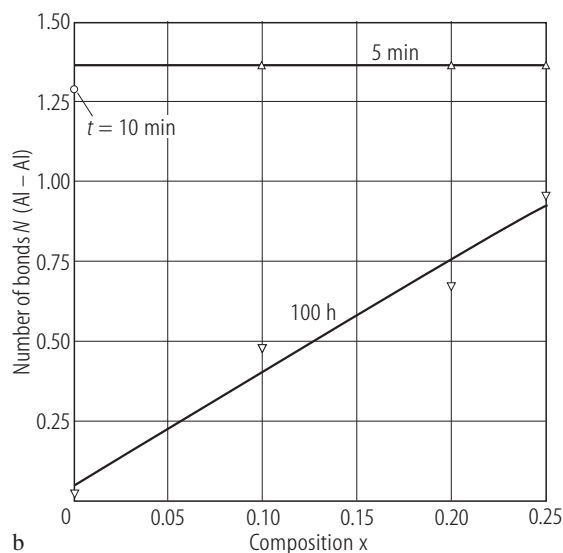
**Fig. 15.** Cordierite,  $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$ . A sequence (a-f) of  $^{29}\text{Si}$  NMR spectra of synthetic samples annealed for increasing time [87P2]. In (a) the large number of Si(nAl) environments is due to the disorder in the first formed hexagonal phase, while in (f) the orthorhombic cordierite is well ordered.



**Fig. 16.** Cordierite,  $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$ . The number of Al–O–Al bonds per formula unit plotted as function of annealing time at three different temperatures [87P2].

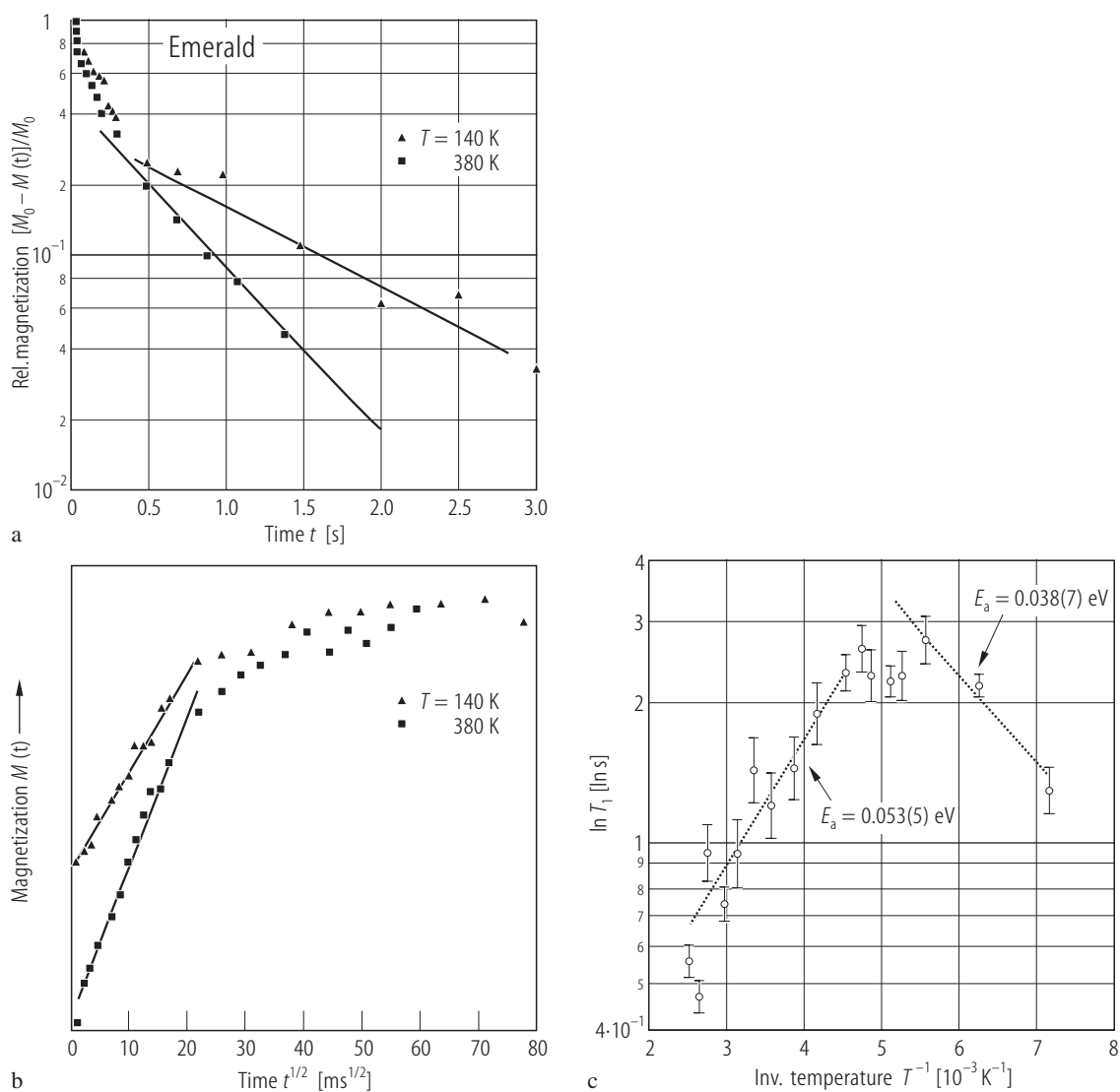


a

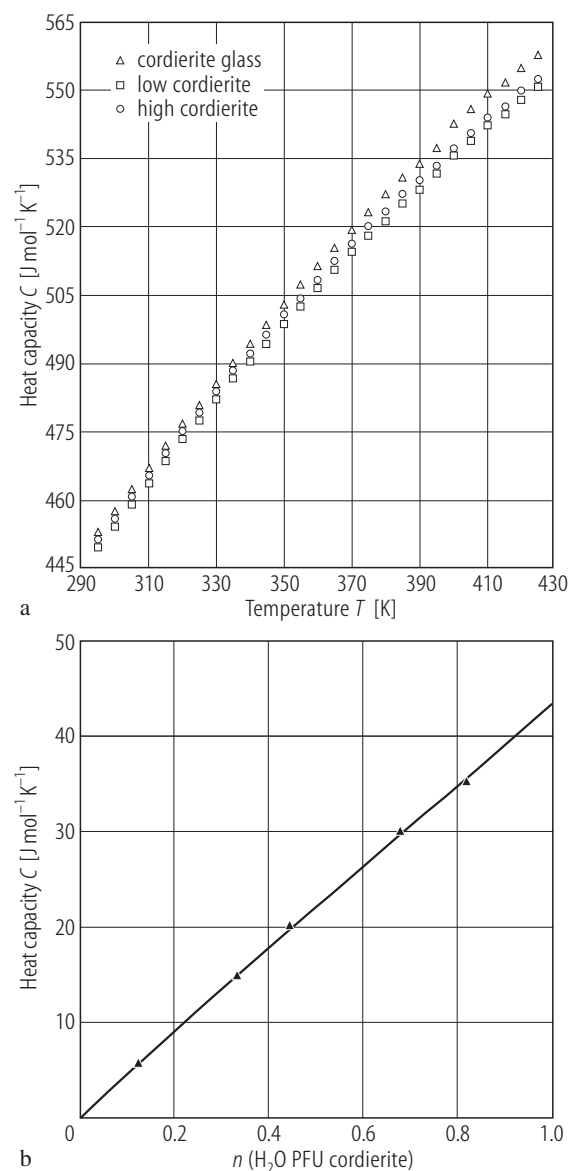


b

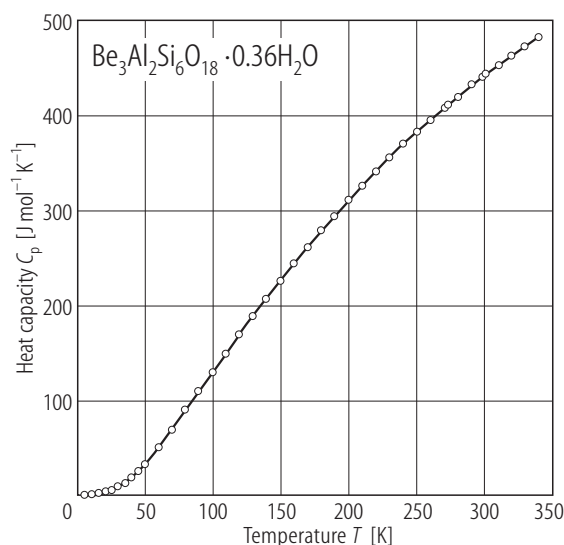
**Fig. 17.**  $\text{K}_x\text{Mg}_2\text{Al}_{4+x}\text{Si}_{5-x}\text{O}_{18}$  cordierites. **(a)** The number of Al–O–Al bonds per formula unit for samples with  $x = 0$  and  $x = 0.25$  as a function of the logarithm of annealing time. The speed of ordering is much slower for cordierites with  $x = 0.25$  than for  $x = 0$ . The estimated errors of all values shown are  $\pm 0.03$ . **(b)** The number of Al–O–Al bonds per formula unit after two different annealing times as a function of the K-concentration [92D1].



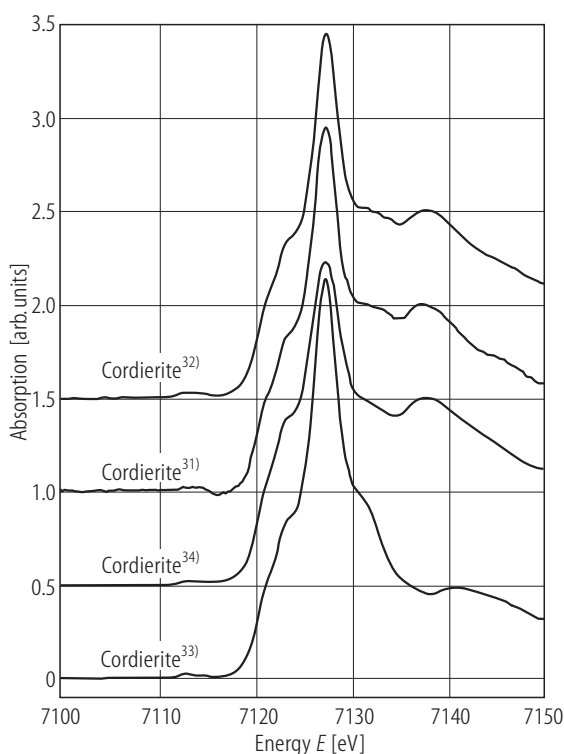
**Fig. 18.** Emerald<sup>40)</sup> single crystal. Data obtained from  $^{27}\text{Al}$  NMR. **(a)** The reduced magnetization (represented by the signal intensity in logarithmic scale) versus delay time,  $t$ . **(b)** The magnetization recovery curves at 140 and 380 K.  $M_0$  is the saturated magnetization when the delay time is long enough [00K1]. **(c)** Temperature dependence of the spin-lattice relaxation time of the  $^{27}\text{Al}$  nucleus. The activation energies are also given [00K1].



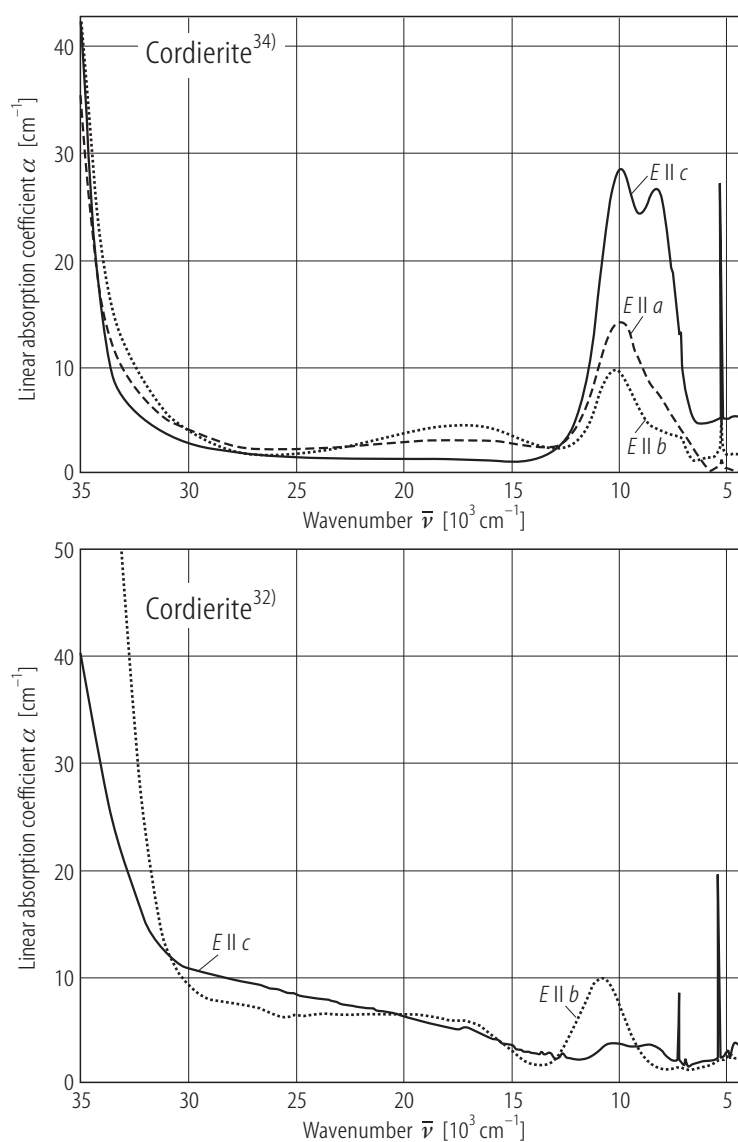
**Fig. 19.** Cordierites. (a) Heat capacity data for high and low structural state and glass from 295 to 425 K. (b) The difference in heat capacity between hydrous and anhydrous samples as function of  $\text{H}_2\text{O}$  content [93C1]. All data between 295 K and 425 K are included in the plot.



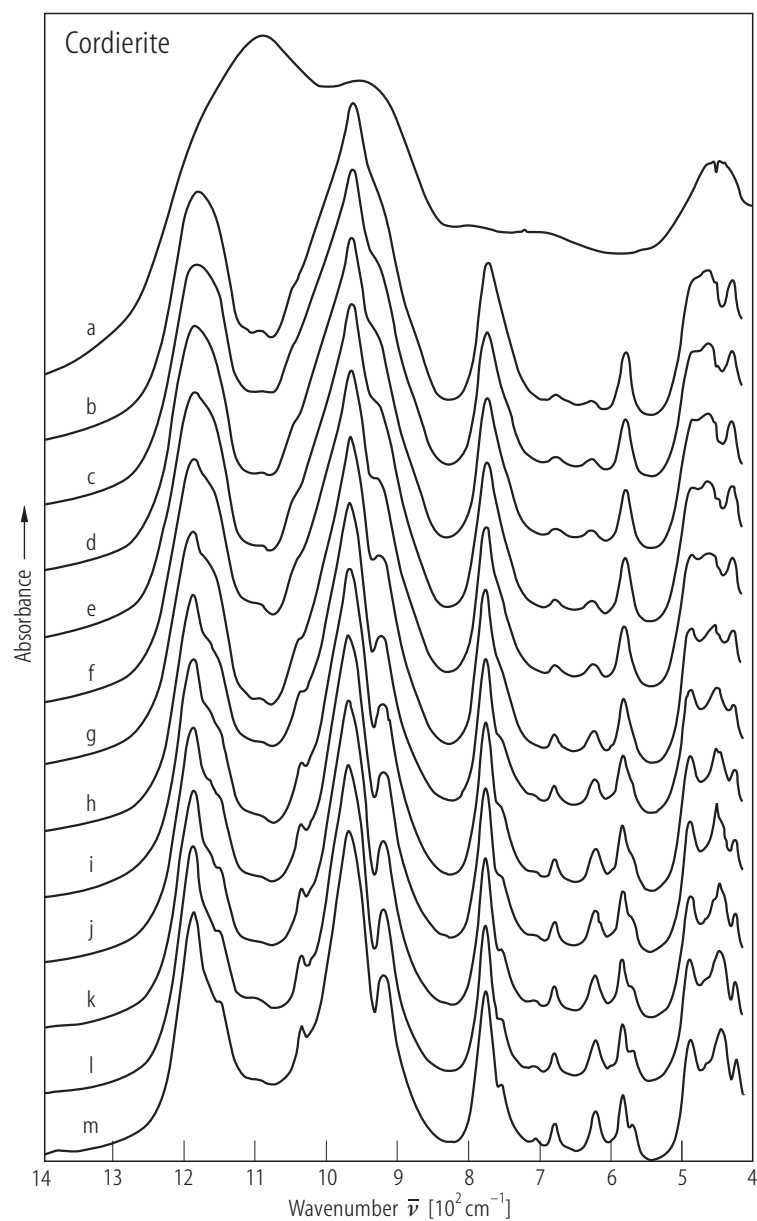
**Fig. 20.** Beryl. Temperature dependence of heat capacity [86H2].



**Fig. 21.** Natural cordierites<sup>31...34</sup>. XAS spectra at room temperature [00G1] (for compositions <sup>31...34</sup> see Table 3).

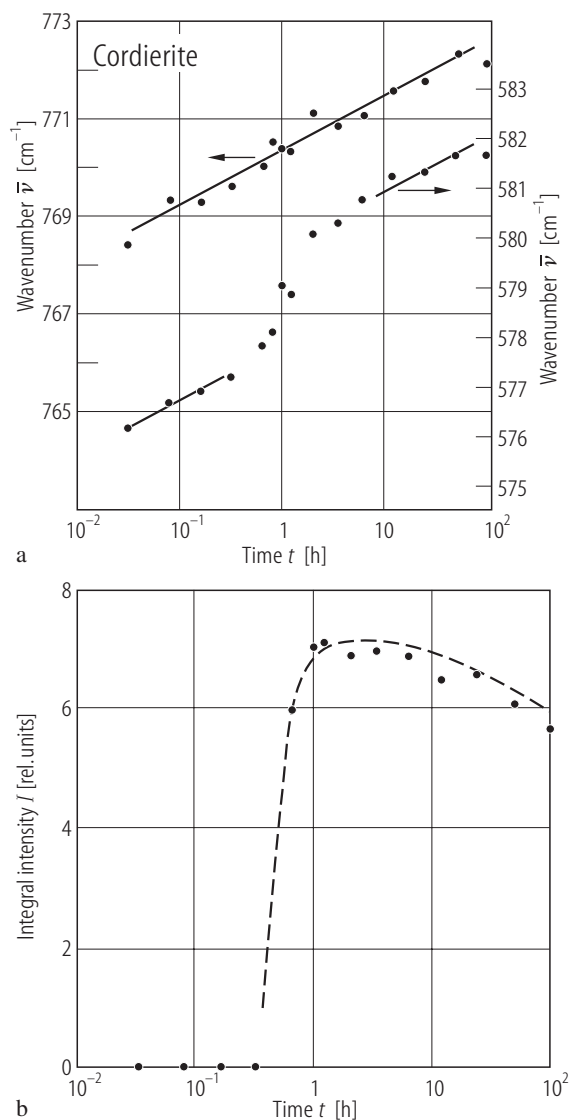


**Fig. 22.** Natural cordierites<sup>32,34)</sup>. Room-temperature polarized absorption spectra. The polarized directions are *a*, *b*, *c* [00G1] (for footnotes (compositions)<sup>32,34)</sup> see Table 3).

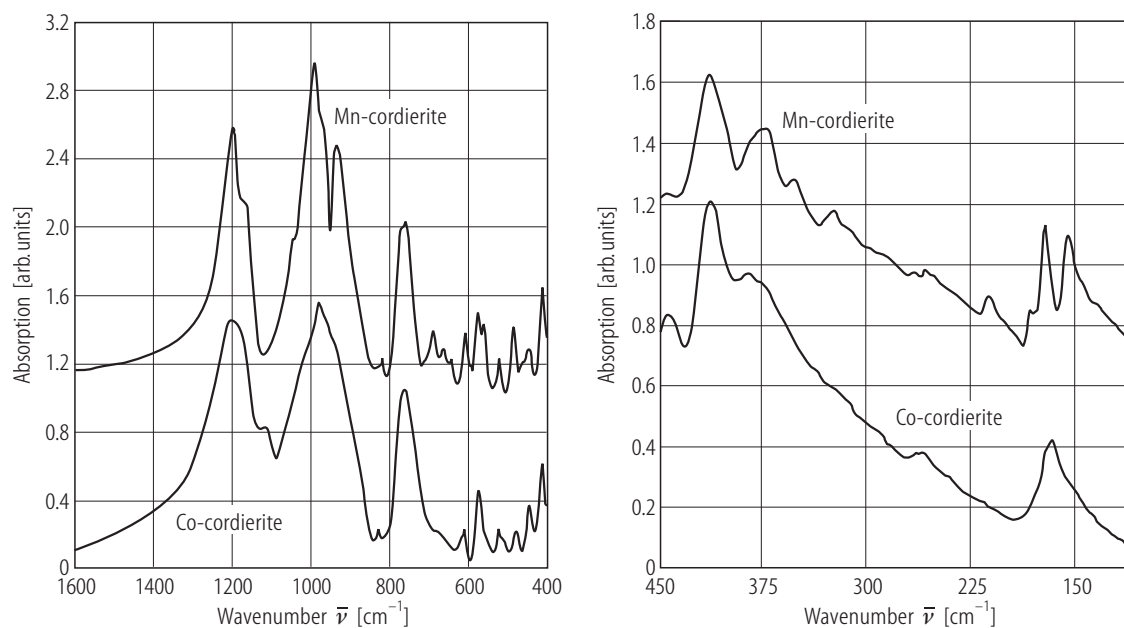


**Fig. 23.** Mg-cordierite glass and crystalline. IR spectra at RT of glass **(a)** and samples annealed at 1290°C for different duration: **(b)**  $t = 2$  min.; **(c)**  $t = 5$  min.; **(d)**  $t = 10$  min.; **(e)**  $t = 20$  min.; **(f)**  $t = 40$  min.; **(g)**  $t = 1$  h; **(h)**  $t = 3$  h; **(i)**  $t = 6$  h; **(j)**  $t = 12$  h; **(k)**  $t = 24$  h; **(l)**  $t = 48$  h; **(m)**  $t = 96$  h. The symmetry of the cordierite samples is hexagonal for **b, c, d, e**, modulated for **f, g, h**, and orthorhombic for **i, j, k, l, m** [89G2].



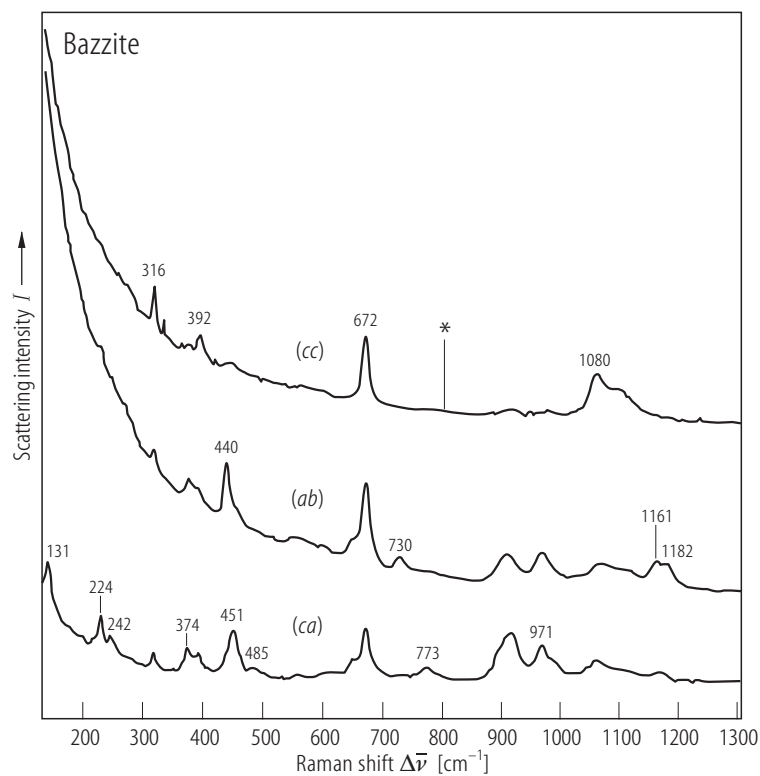


**Fig. 24.** Mg-cordierite. **(a)** Frequency shift versus logarithmic annealing time of the modes near  $770 \text{ cm}^{-1}$  and  $580 \text{ cm}^{-1}$  (from room-temperature measurements). **(b)** Integrated intensity vs logarithmic annealing time of the mode near  $568 \text{ cm}^{-1}$  as deduced by line profile analysis of the 80 K measurements [89G2].

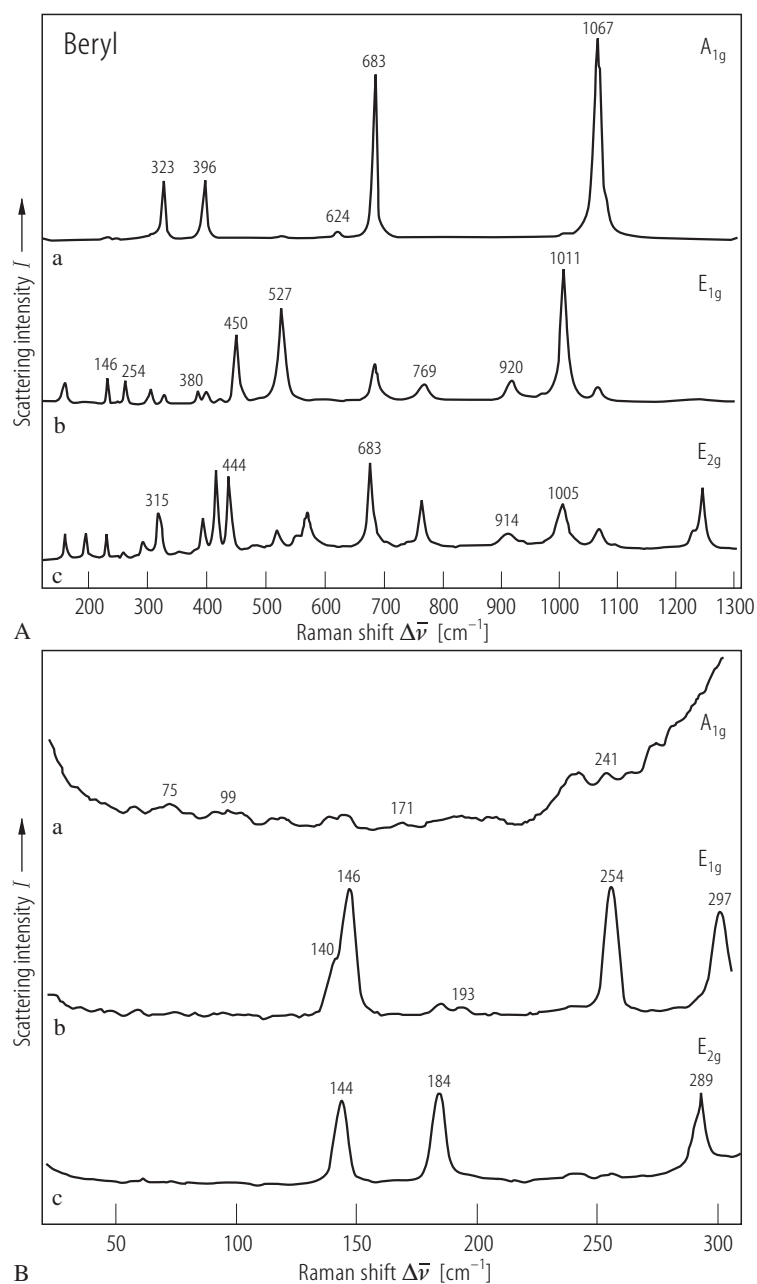


**Fig. 25.** Mn- and Co-cordierites. FTIR absorption spectra from 80...1600  $\text{cm}^{-1}$ . The difference in the width of the absorption bands is due to the different ordering states [99K1].

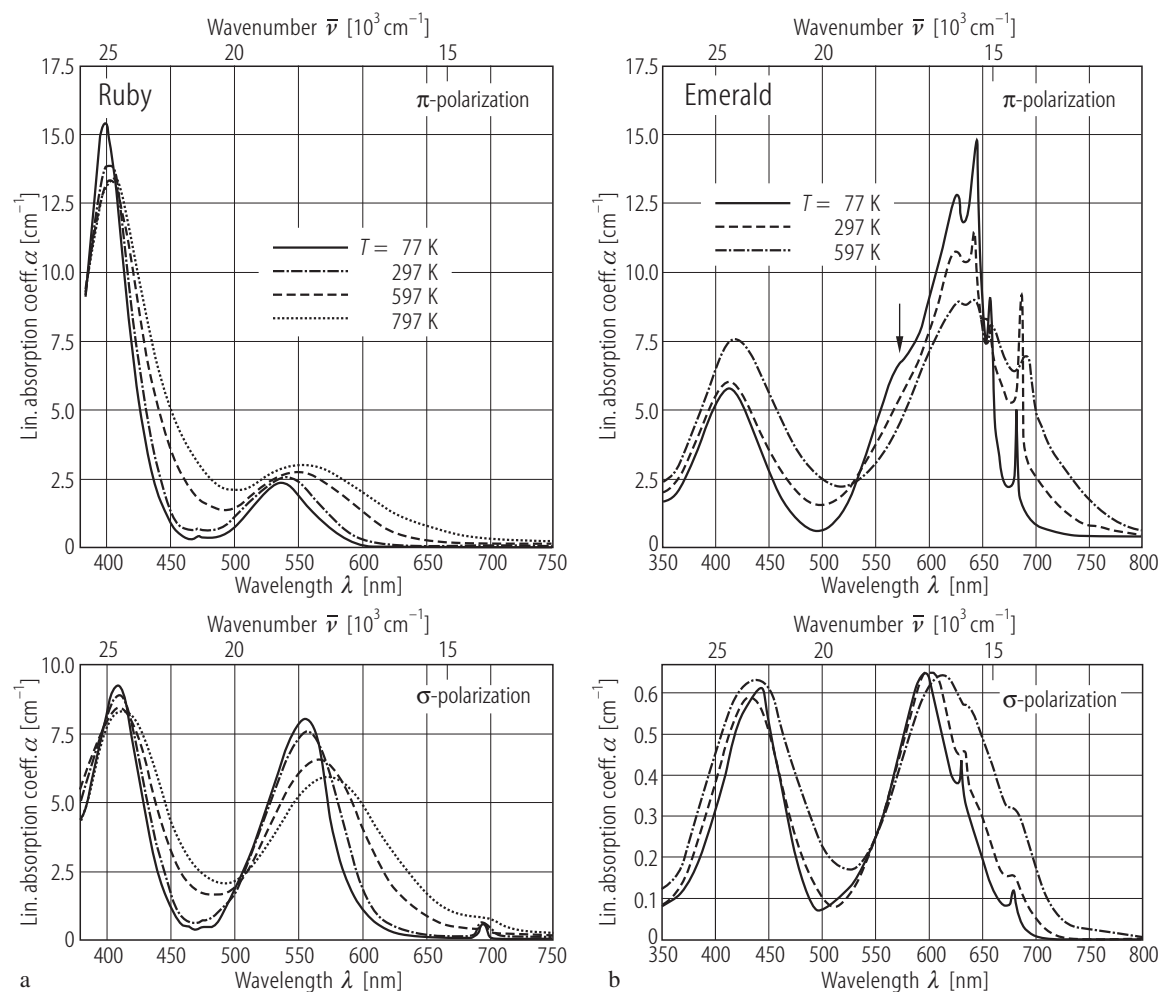
For Fig. 26 see next page



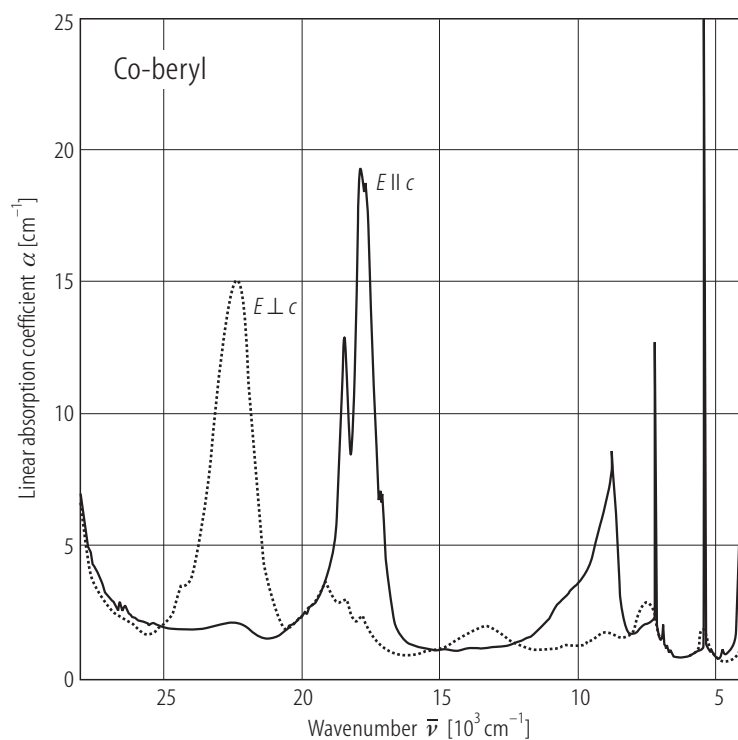
**Fig. 27.** Bazzite. Polarized Raman spectra at room temperature. The sharp peak marked \* is an artefact and does not belong to the spectrum [90H1].



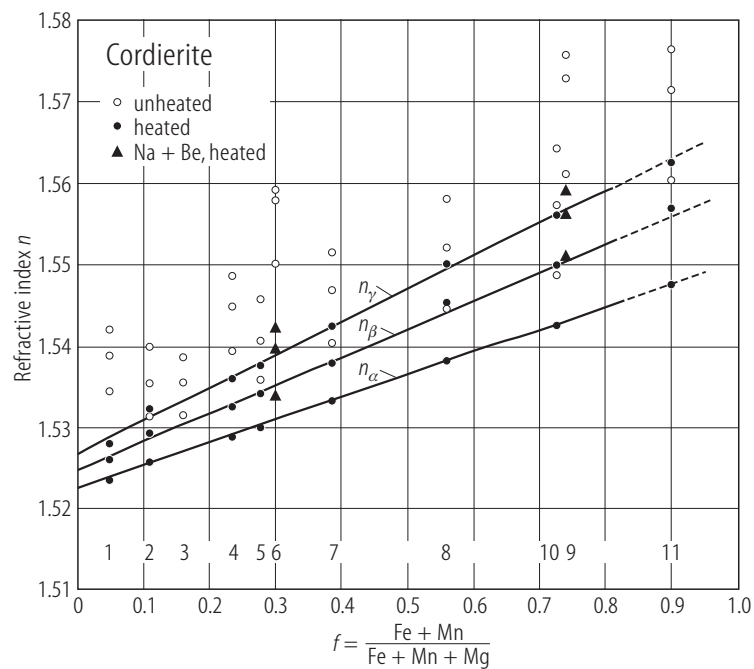
**Fig. 26.** Beryl. Polarized Raman spectra at room temperature in: **(a)**  $A_{1g}$  symmetry (polarization  $cc$ ), **(b)**  $E_{1g}$  symmetry (polarization  $ca$ ), **(c)**  $E_{2g}$  symmetry (polarization  $ba$ ) [90H1]. (Sample: synthetic flux grown emerald (0.73 wt %  $Cr_2O_3$ )).



**Fig. 28.** Ruby (a) and emerald (b). Polarized spectra  $E \parallel c$  ( $\pi$ ) and  $E \perp c$  ( $\sigma$ ) in the temperature range 77 to 597 K [94T1].



**Fig. 29.** Co-bearing beryl. Polarized optical absorption spectra [01T1].



**Fig. 30.** Cordierites. Refractive indices  $n_\alpha$ ,  $n_\beta$  and  $n_\gamma$  versus atomic ratio  $f$  for unheated cordierite grains 1 to 11 (open circles) and for the same grains after heating at 800°C for six hours (filled circles or triangles) [80S1].