No. 1A-7 $CaTiO_3$, Calcium titanate

(M = 135.98)

1a Specific heat anomaly associated with a phase transition was observed in $CaTiO_3$ at about 1260°C by Naylor et al. in 1946. 46Nay
Granicher et al. reported that $CaTiO_3$ becomes cubic above 1260 °C. 54Gra

b

phase	II	I
state	P	
crystal system	orthorhombic [b])	cubic [a])
space group	Pbmn – D_{2h}^{16}	Pm3m – O_h^1
Θ [°C]	≈ 1260	

[a]) 54Gra
[b]) 57Kay
46Nay

$\rho = 4.10 \cdot 10^3$ kg m^{-3} at RT. 62Mer
T_{melt} = 1960°C. 62Mer
The ideal perovskite cubic unit cell becomes pseudo-monoclinic in phase II in the same manner as shown in Fig. 1A-4-001. $\beta' = 90°\ 48'$ at RT.
Transparent, colorless. 57Kay

2 Crystal growth: flux method. [a]) 57Kay
(flux: $CaCl_2$, $BaCl_2$, $CaCl_2$+$BaCl_2$, $NaCO_3$+K_2CO_3) [a]), flame fusion method [b]), firing of mixed oxide [c]), hydrothermal synthesis [d]). [b]) 58Lin, 62Mer
[c]) 88Lar
[d]) 95Len

3a a = 5.388(1) Å, b = 5.447(1) Å, c = 7.654(1) Å at RT. 92But
Unit cell parameters: Table 3. 57Kay

b Z = 1 in phase I and Z = 4 in phase II. 57Kay
Crystal structure: Fig. 1A-7-001, Table 1A-7-001.
See also: 83Koo
Interatomic distances and angles: Table 1A-7-002; see also 92But

4 Lattice distortion: Fig. 1A-7-002.
Thermal expansion: see 92Bal

5a Dielectric constant: $\kappa' = 186$, $\tan\delta = 3 \cdot 10^{-4}$ at RT (f = 1 kHz). Fig. 1A-7-003. 58Lin

6a Heat capacity: Fig. 1A-7-004.
Transition heat: $\Delta Q_m = 2.30 \cdot 10^3$ J mol^{-1} at Θ_{II-I}. 46Nay

9a Refractive indices: Fig. 1A-7-005.
Reflection and absorption: Fig. 1A-7-006.
Optical absorption coefficient: Fig. 1A-7-007.
Complex dielectric constant: Fig. 1A-7-008.
Birefringence: Fig. 1A-7-009.

10a Raman spectra of $Ca_{1-x}Gd_xTiO_3$: Fig. 1A-7-010.

11 Electronic structure: see 81Roz
Ti: L_{II-III}, O: K-level; X-ray photoemission: see 83Shv

13b EPR: see 89Bol

14c EXAFS: see 88Lar

15a	Domain structure: Fig. 1A-7-011.	93Ceh
16	Hardness: Mohs 6.5...7, Knoop 986.	62Mer

Table 1A-7-001. $CaTiO_3$. Structure of phase II [57K1]. Fractional coordinates of atoms in the unit cell.

4 Ti in 4(a):	1/2, 0, 0; 0, 0, 1/2; 1/2, 1/2, 0; 0, 1/2, 1/2.
4 Ca in 4(c):	x, 1/4, z; $\bar{x}$, 3/4, $\bar{z}$; 1/2+x, 3/4, 1/2–z; 1/2–x, 1/4, 1/2+z; with x = 0, z = 0.030.
4 O in 4(c):	with x = 1/2–0.037, z = –0.018.
8 O in 8(d):	x, y, z; 1/2–x, 1/2–y, 1/2+z; $\bar{x}$, 1/2+y, $\bar{z}$; 1/2+x, $\bar{y}$, 1/2–z; $\bar{x}$, $\bar{y}$, $\bar{z}$; 1/2+x, 1/2+y, 1/2–z; x, 1/2–y, z; 1/2–x, y, 1/2+z; with x = 1/4–0.018, y = –0.026, z = 1/4–0.018.

Table 1A-7-002. $Ca_{0.925}Ga_{0.075}TiO_3$. Interatomic distances and angles [88Lar].

	Ti–O [Å]	Ca(Gd)–O [Å]	O–Ti–O [°]
O1	$1.949(1) \times 2$	2.371(5)	89.2(1)–90.5(1)
O1'		2.485(5)	
O2	$1.952(3) \times 2$	$2.614(4) \times 2$	
O2'	$1.959(3) \times 2$	$2.394(4) \times 2$	
O2"		$2.670(4) \times 2$	

Table 1A-7-003. $Ca_{0.925}Gd_{0.075}TiO_3$ and $CaTiO_3$. Unit cell parameter [88Lar].

	a [Å]	*b* [Å]	*c* [Å]	*V* [Å^3]
$CaTiO_3$ [a])	5.3829(3)	5.4458(3)	7.6453(3)	224.12
$(Ca_{0.92}Gd_{0.075})TiO_3$	5.381(1)	5.449(1)	7.647(1)	224.22
	x	*y*	*z*	B_{iso}
Ca(Gd)	0.0066(2)	0.0350(2)	1/4	0.97
Ti	1/2	0	0	0.46
O1	0.5689(9)	–0.0150(8)	1/4	0.46
O2	0.2870(6)	0.2870(5)	0.0350(2)	0.76

[a]) [83Koo].

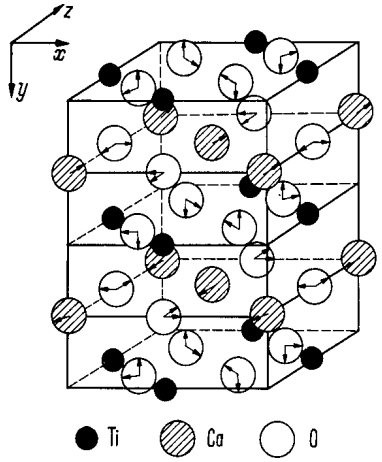

Fig. 1A-7-001. $CaTiO_3$. A sketch of the structure in phase II [57Kay]. Displacements of the atoms from the positions of the ideal cubic perovskite structure are indicated by arrows. See Table 1A-7-001.

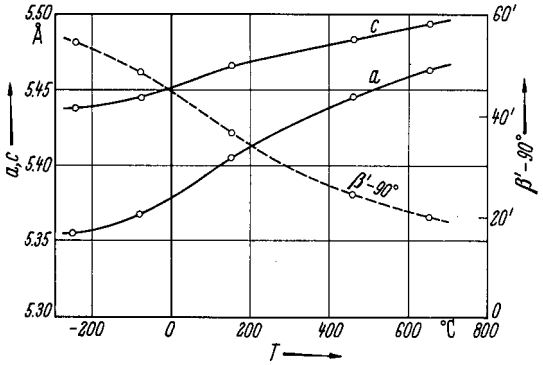

Fig. 1A-7-002. $CaTiO_3$. a, c and β'–90° vs. T [57Kay].

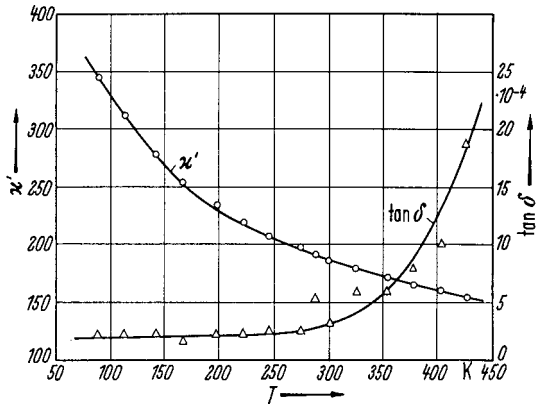

Fig. 1A-7-003. $CaTiO_3$. κ', $\tan\delta$ vs. T [58Lin]. f = 1 kHz.

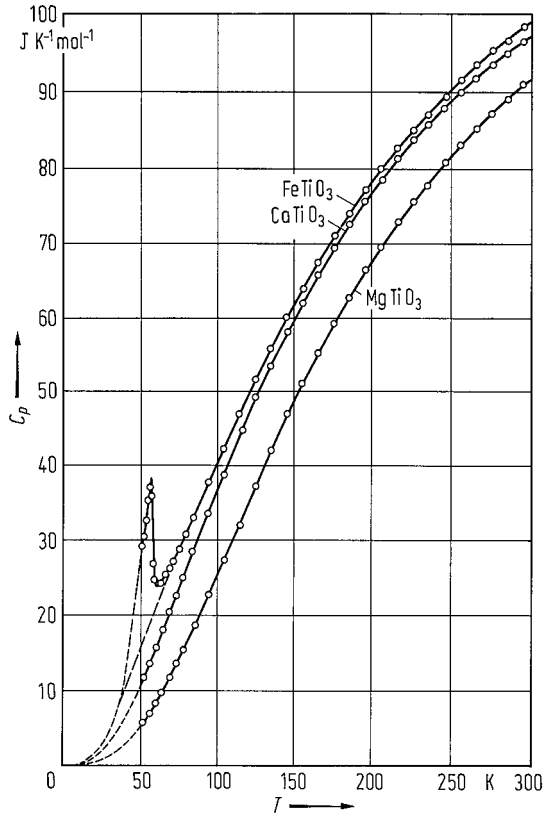

Fig. 1A-7-004. $CaTiO_3$, $FeTiO_3$, $MgTiO_3$. C_p vs. T [46Sho].

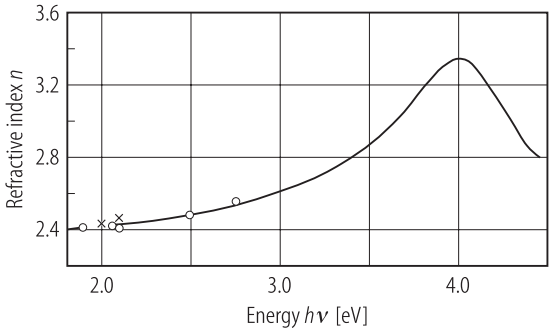

Fig. 1A-7-005. $CaTiO_3$. n vs. $h\nu$ at RT [80Yak]. The solid curve: refractive index n obtained from the reflectivity data; the crosses: obtained from the interference experiment with a thin crystal; the circles: data of [58Lin].

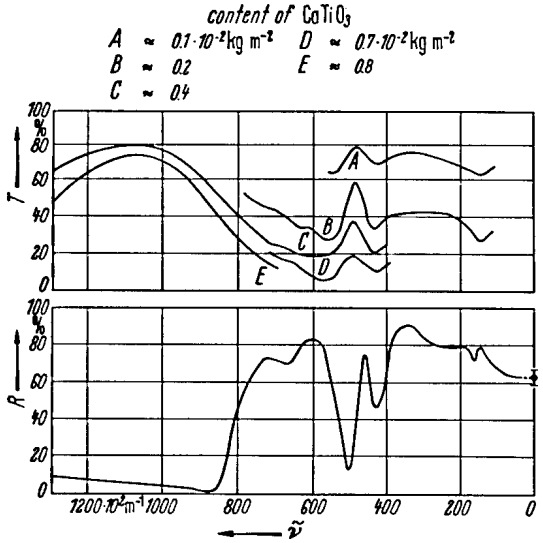

Fig. 1A-7-006. $CaTiO_3$. *T* and *R* vs. $\tilde{\nu}$ [64Per]. *T*: transmittance, *R*: reflectance. Matrix: KBr and polyethylene.

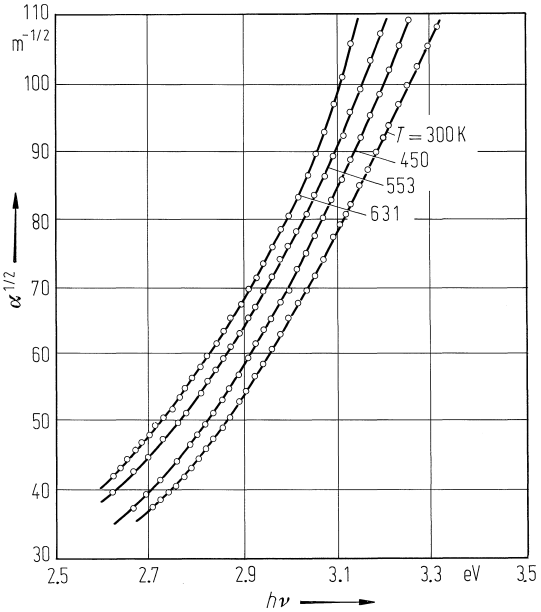

Fig. 1A-7-007. $CaTiO_3$. $\alpha^{1/2}$ vs. $h\nu$ [80Yak]. Parameter: T.
α: optical absorption coefficient, $h\nu$: photon energy.

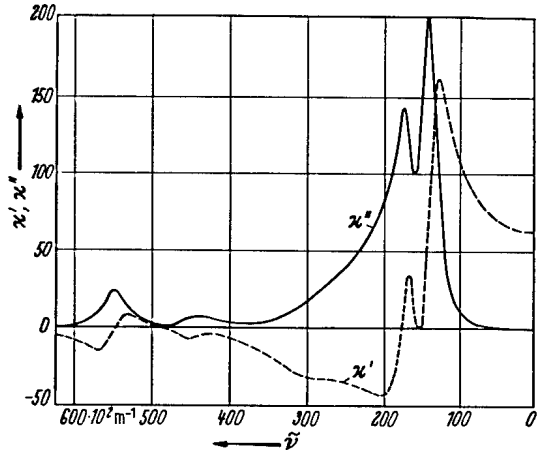

Fig. 1A-7-008. $CaTiO_3$. κ' and κ'' vs. $\tilde{\nu}$. Calculated from the reflectivity data using Kramers-Kronig relation [64Per].

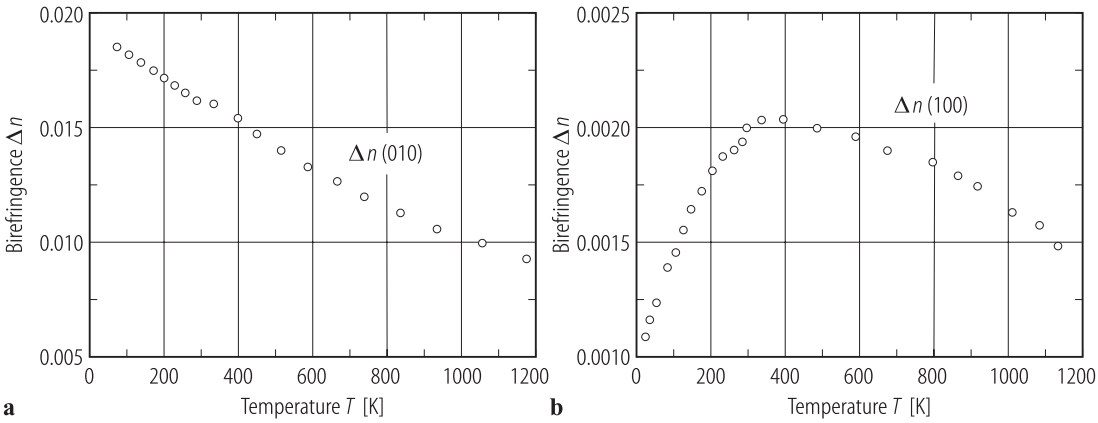

Fig. 1A-7-009. $CaTiO_3$. Δn vs. T [87ElM]. Measurements were made on planes correlated to the pseudocubic axis (λ = 632.8 nm). (**a**) Δn (010), (**b**) Δn (100).

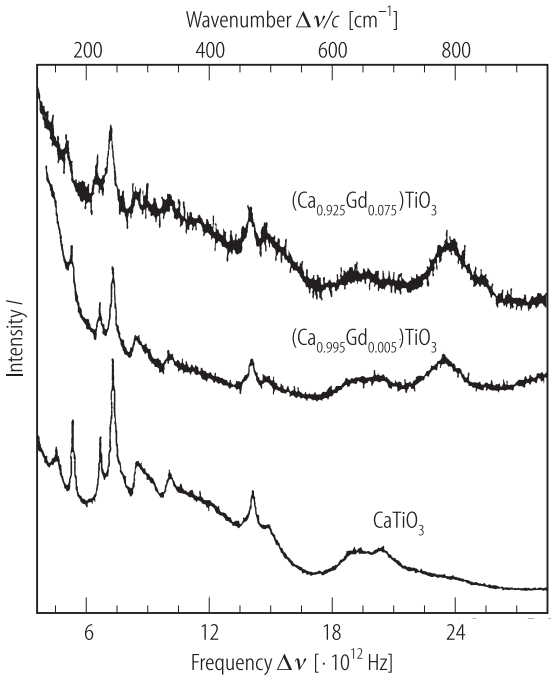

Fig. 1A-7-010. $Ca_{1-x}Gd_xTiO_3$ and $CaTiO_3$. Raman spectra [88Lar]. Parameter: x.

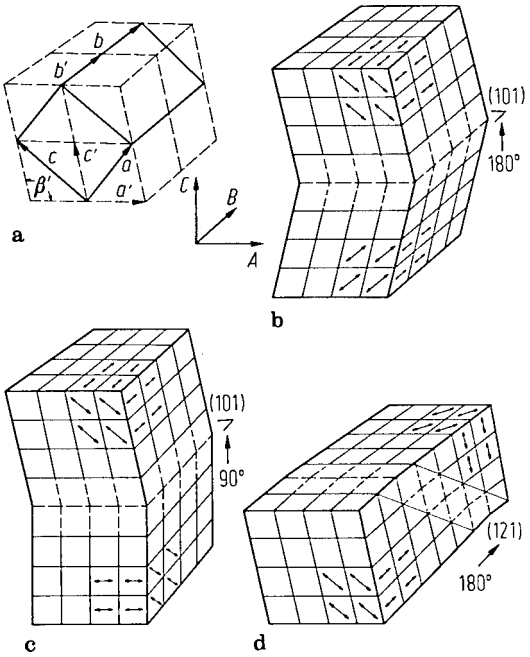

Fig. 1A-7-011. $CaTiO_3$. Possible domain configuration in orthorhombic cell [57Kay]. **(a)** Orthorhombic unit cell (full line) and the cell edges *a*, *b*, *c* in relation to sheared pseudocubic primitive cells (broken line) with *a*', *b*', *c*', ß'. **(b)** Most common form of twinning by rotation about normal to (101) with composition plane (101). **(c)** Twinning by rotation of 90° about normal to (101) with composition plane (101). **(d)** Twinning by rotation of 180° about normal to (121) with composition plane (121).

References

46Nay Naylor, B.F., Cook, O.A.: J. Am. Chem. Soc. **68** (1946) 1003.
46Sho Shomate, C.H.: J. Am. Chem. Soc. **68** (1946) 964.
54Gra Granicher, H., Jakits, O.: Nouvo Cimento [9] **11**, Suppl. (1954) 480.
57Kay Kay, H.F., Bailey, P.C.: Acta Crystallogr. **10** (1957) 219.
58Lin Linz, A., Herrington, K.: J. Chem. Phys. **28** (1958) 824.
62Mer Merker, L.: J. Am. Ceram. Soc. **45** (1962) 366.
64Per Perry, C.H., Khanna, B.N., Rupprecht, G.: Phys. Rev. **135** (1964) A408.
80Yak Yakubovskii, M.A., Zametin, V.I., Rabkin, L.M., Fesenko, E.G.: Fiz. Tverd. Tela **22** (1980) 3523; Sov. Phys. Solid State (English Transl.) **22** (1980) 2064.
81Roz Rozova, M.N., Onopko, D.E., Titov, S.A., Kostikov, Yu.P.: Fiz. Tverd. Tela **23** (1981) 1704; Sov. Phys. Solid State (English Transl.) **23** (1981) 992.
83Koo Koopman, H.J., Van de Velde, G.M.H., Gellings, P.J.: Acta Crystallogr., Sect. C **39** (1983) 1323.
83Shv Shveitser, I.G., Mazuritskii, M.I., Prokopalo, O.I.: Fiz. Tverd. Tela **25** (1983) 2273; Sov. Phys. Solid State (English Transl.) **25** (1983) 1305.
87ElM El-Mallah, H., Watts, B.E., Wanklyn, B.: Phase Transitions **9** (1987) 235.
88Lar Larson, E.M., Eller, P.G., Purson, J.D., Pace, C.F.: J. Solid State Chem. **73** (1988) 480.
89Bol Boldú, J.L., Boatner, L.A., Abraham, M.M.: J. Chem. Phys. **91** (1989) 5117.
92Bal Ball, C.J., Thorogood, G.J., Vance, E.R.: J. Nucl. Mater., **190** (1992) 298.
92But Butlner, R.H., Maslen, E.N.: Acta Crystallogr., Sect. B **48** (1992) 644.
93Ceh Ceh, M., Krasevec, V.: J. Solid State Chem. **103** (1993) 263.
95Len Lencka, M.M., Riman, R.E.: Chem. Mater. **7** (1995) 18