54 $CH_3NH_3AlCl_4$ family

54A Pure compounds

No. 54A-1 $CH_3NH_3AlCl_4$, Methylammonium tetrachloroaluminate
(M = 200.86)

1a Ferroelectric activity in $CH_3NH_3AlCl_4$ was discovered by Czapla et al. in 1986. 86Cza

b 86Cza

phase	II	I
state	F	(P)
crystal system		tetragonal
space group		$I4-C_4^5$ or $I\bar{4}-S_4^2$
Θ [K]	100	

$P_s \parallel a$. 86Cza

2a Crystal growth: evaporation method from an aqueous solution of the stoichiometric amounts of CH_3NH_3Cl and $AlCl \cdot 6H_2O$. 86Cza
Crystal form: Fig. 54A-1-001.
Cleavage plane: perpendicular to c. 86Cza

3a Unit cell parameters: a = 6.3 Å, c = 20.4 Å at RT. 86Cza

5a Dielectric constants: Fig. 54A-1-002.
$\kappa_a = C_p/(T - \Theta_f)$, $T > \Theta_f$ with Θ_f = 100 K, C_p = 700 K; 86Cza
$\kappa_a = C_f/(\Theta_f - T)$, $T < \Theta_f$ with C_f = 380 K.
Dielectric dispersion: Fig. 54A-1-003, Fig. 54A-1-004, Fig. 54A-1-005, Fig. 54A-1-006.

c Spontaneous polarization and coercive field: Fig. 54A-1-007.

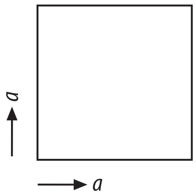

Fig. 54A-1-001. $CH_3NH_3AlCl_4$. Section perpendicular to ***c*** of the crystal form [86Cza].

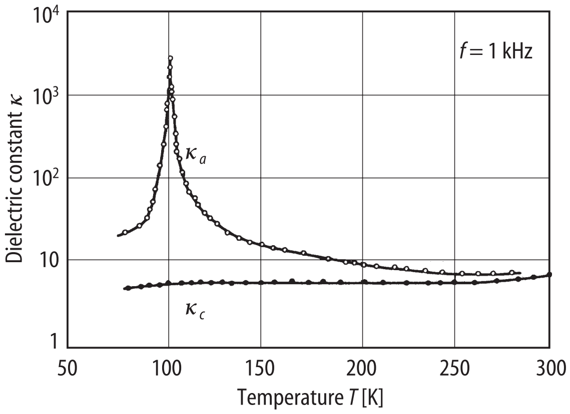

Fig. 54A-1-002. $CH_3NH_3AlCl_4$. κ_a, κ_c vs. T [86Cza].

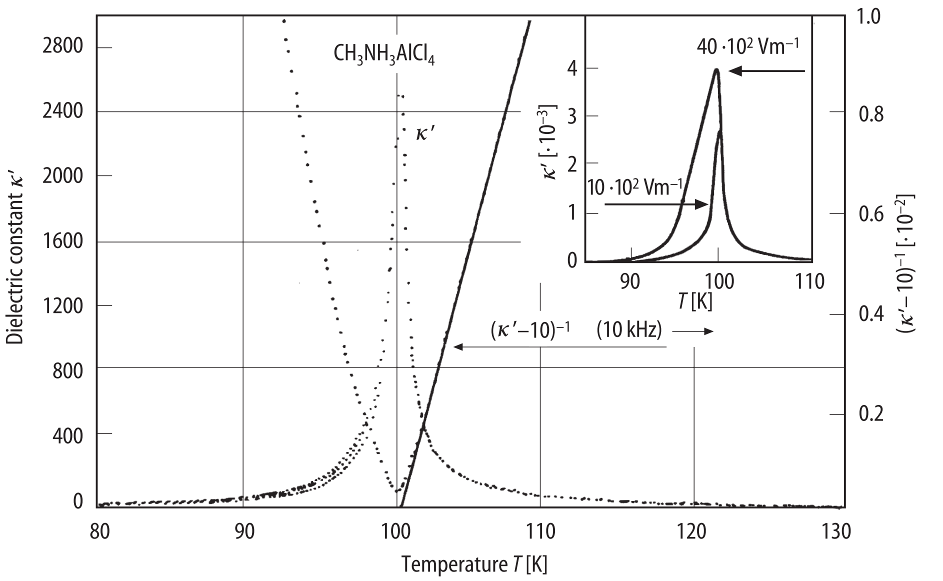

Fig. 54A-1-003. $CH_3NH_3AlCl_4$. κ', $(\kappa'-10)^{-1}$ vs. T at a measuring field strength of about 10^2 Vm^{-1} [90Paw]. Parameter: f = 10 kHz, 100 kHz, 1 MHz, showing a dispersion in the ferroelectric phase, but no dispersion in the paraelectric phase. The curves in the ferroelectric phase correspond to those of 10 kHz, 100 kHz, 1 MHz from the lower side. Insert: κ' vs. T. Parameter: measuring field strength $10 \cdot 10^2$ Vm^{-1}, $40 \cdot 10^2$ Vm^{-1}.

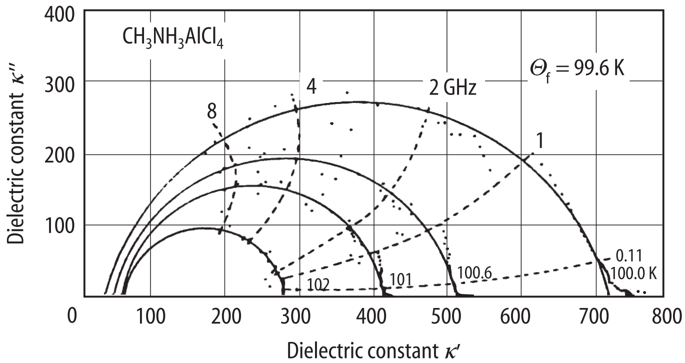

Fig. 54A-1-004. $CH_3NH_3AlCl_4$. Cole-Cole plots in the paraelectric phase [90Paw]. Parameter: T = 100.0 K, 100.6 K, 101 K, 102 K.

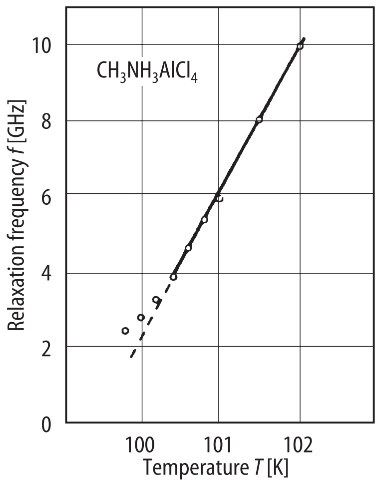

Fig. 54A-1-005. $CH_3NH_3AlCl_4$. f vs. T in the paraelectric phase [90Paw]. f: relaxation frequency.

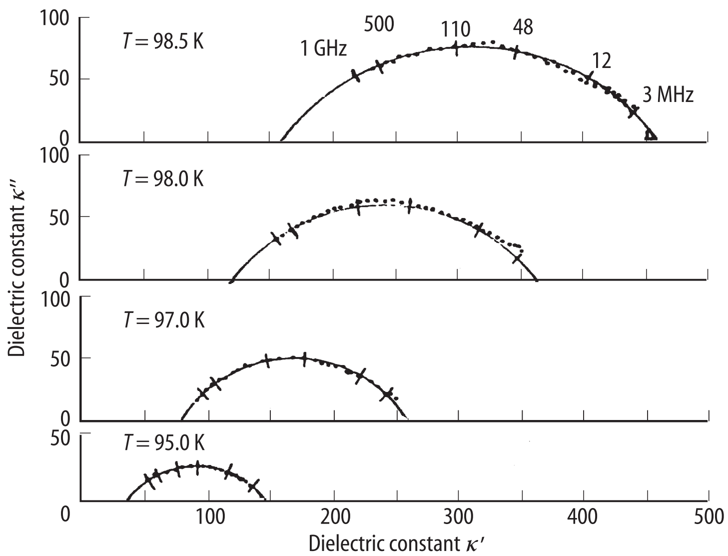

Fig. 54A-1-006. $CH_3NH_3AlCl_4$. Cole-Cole plots in the ferroelectric phase [90Paw]. Parameter: T = 98.5 K, 98.0 K, 97.0 K, 95.0 K.

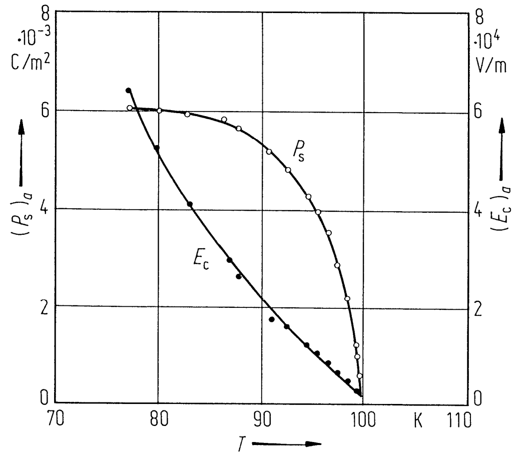

Fig. 54A-1-007. $CH_3NH_3AlCl_4$. $(P_s)_a$, $(E_c)_a$ vs. T [86Cza]. $(P_s)_a$, $(E_c)_a$: spontaneous polarization and coercive field along ***a***.

References

86Cza Czapla, Z., Czupiński, O., Ciunik, Z.: Solid State Commun. **58** (1986) 383.
90Paw Pawlaczyk, C., Unruh, H.G., Czapla, Z.: Ferroelectrics **108** (1990) 133.

No. 54A-2 $(CH_3NH_3)_2AlCl_5 \cdot 6H_2O$, Methylammonium aluminum chloride hexahydrate

(M = 376.49)

1a	This material is considered to be the identical substance to No. 54A-1 ($CH_3NH_3AlCl_4$). Reexamination of the chemical formula by a chemical analysis showed that it should be revised as $(CH_3NH_3)_2AlCl_5 \cdot 6H_2O$.				97Ono
b	phase	III	II	I	
	Θ [K]	100.0	307		97Ono
6a	Transition heat and entropy: Table 54A-2-001. Specific heat and excess specific heat at phase transition: Fig. 54A-2-001, Fig. 54A-2-002. Excess entropy at the two transition points: Fig. 54A-2-003, Fig. 54A-2-004.				

Table 54A-2-001. $(CH_3NH_3)_2AlCl_5 \cdot 6H_2O$. Transition heats and transition entropies associated with the two transition points [97Ono].

T [K]	ΔH [kJ mol^{-1}]	ΔS [J K^{-1} mol^{-1}]
100.0(1)	0.20	2.18
307.0(1)	1.48	4.85

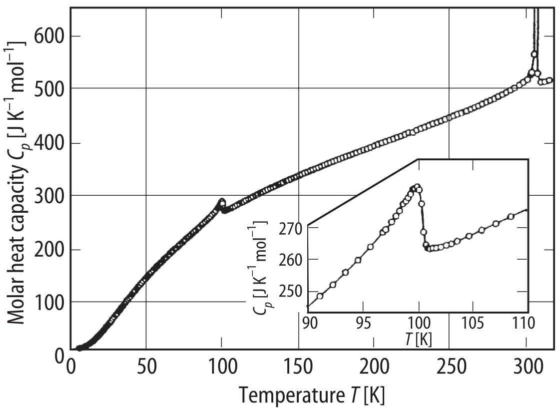

Fig. 54A-2-001. $(CH_3NH_3)_2AlCl_5 \cdot 6H_2O$. C_p vs. T [97Ono]. Insert: C_p around Θ_{III-II}.

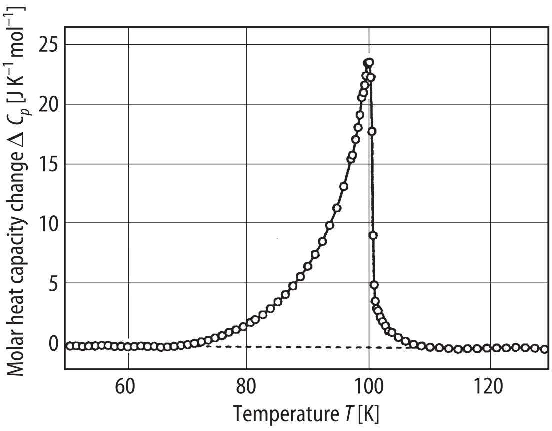

Fig. 54A-2-002. $(CH_3NH_3)_2AlCl_5 \cdot 6H_2O$. ΔC_p vs. T around Θ_{III-II} [97Ono].

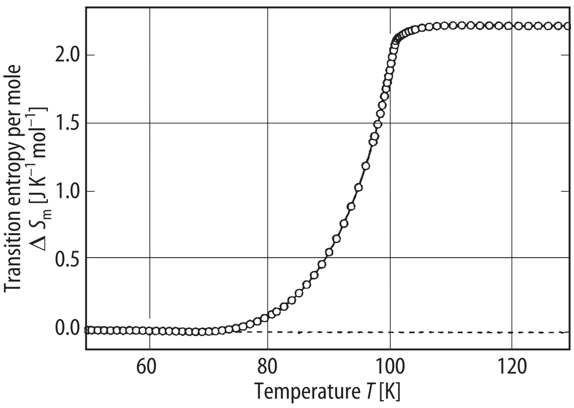

Fig. 54A-2-003. $(CH_3NH_3)_2AlCl_5 \cdot 6H_2O$. ΔS_m vs. T around Θ_{III-II} [97Ono].

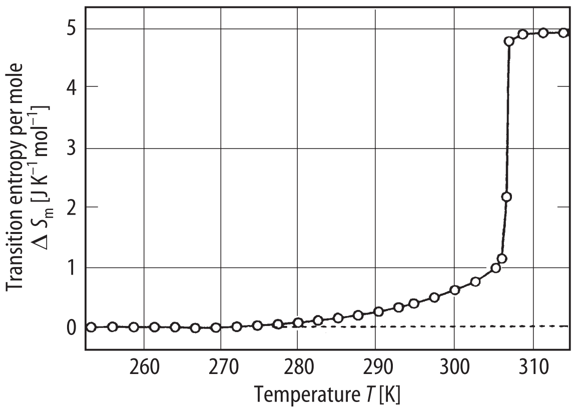

Fig. 54A-2-004. $(CH_3NH_3)_2AlCl_5 \cdot 6H_2O$. ΔS_m vs. T around $\Theta_{II–I}$ [97Ono].

Reference

97Ono Onoda-Yamamuro, N., Ikeda, R., Yamamuro, O., Matsuo, T.: Solid State Commun. **101** (1997) 647.

No. 54A-3 $CH_3NH_3AlBr_4$, Methylammonium tetrabromoaluminate

(M = 378.66)

1a Ferroelectric activity in $CH_3NH_3AlBr_4$ was discovered by Gesi in 1996. 96Ges

b 96Ges

phase	II	I
state	F	P
crystal system		tetragonal
space group		I4/mmm– D_{4h}^{17}
Θ [K]	76.6	

$P_s \parallel \boldsymbol{a}$. 96Ges

2a Crystal growth: evaporation method from an aqueous solution of the stoichiometric amounts of CH_3NH_3B and $AlBr \cdot 6H_2O$. 96Ges

Crystal form: rectangular plate. 96Ges

Colorless, transparent. 96Ges

The crystal habit was the same as that of $CH_3NH_3AlCl_4$. 86Cza

Cleavage plane: perpendicular to c. 96Ges

3a Unit cell parameters: a = 6.616 Å, c = 21.479 Å at RT. 96Mas

b Z = 4.

5a Dielectric constant: $\kappa_a = \kappa_0 + C/(T - T_0)$, $\kappa_0 = 5.0$, $T_0 = 76.8$ K, $C = 3.7 \cdot 10^2$ K. 86Cza

Fig. 54A-3-001, Fig. 54A-3-002, Fig. 54A-3-003.

c Spontaneous polarization and coercive field: $P_s \cong 6.5 \cdot 10^{-3}$ Cm^{-2}, $E_c \cong 1.2 \cdot 10^4$ Vm^{-1} at 64 K. 96Ges

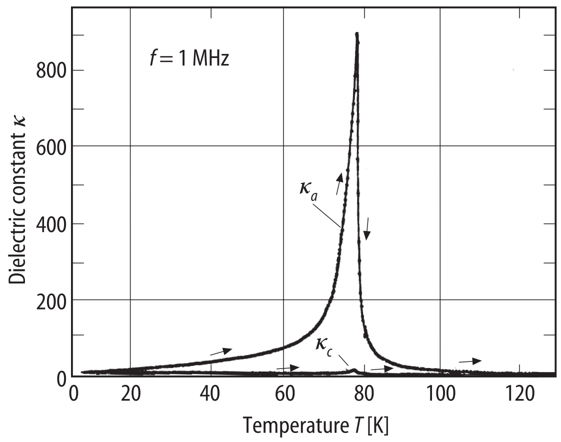

Fig. 54A-3-001. $CH_3NH_3AlBr_4$. κ_a, κ_c vs. T [96Ges]. Strength of measuring field: 5 Vm^{-1}.

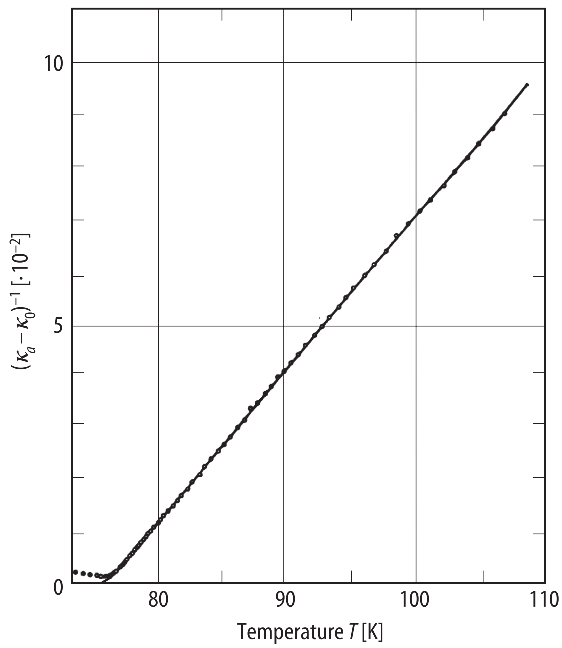

Fig. 54A-3-002. $CH_3NH_3AlBr_4$. $(\kappa_a - \kappa_0)^{-1}$ vs. T [96Ges]. f = 1 MHz. κ_0 = 5.0.

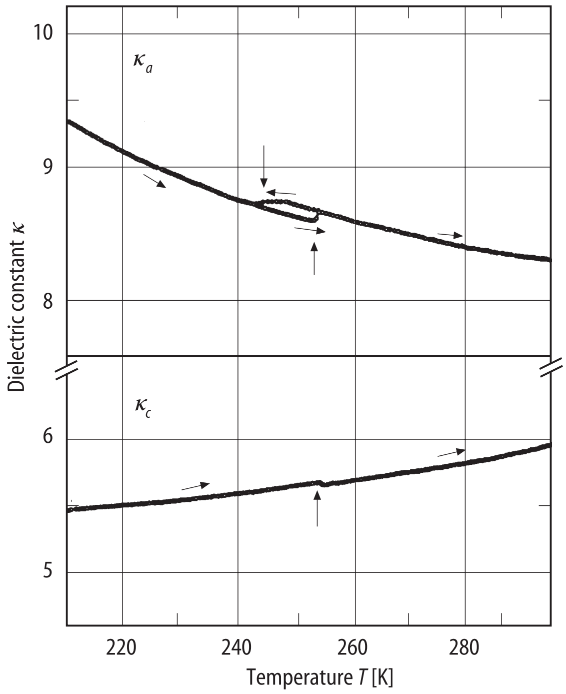

Fig. 54A-3-003. $CH_3NH_3AlBr_4$. κ_a, κ_c vs. T [96Ges]. f = 100 kHz. Anomalies associated with the phase transition are indicated by vertical arrows.

References

86Cza Czapla, Z., Czupiński, O., Ciunik, Z.: Solid State Commun. **58** (1986) 383.
96Ges Gesi, K.: J. Phys. Soc. Jpn. **65** (1996) 703.
96Mas Mashiyama, H.: Private communication (1996), cited in [96Ges].