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# The Dielectric Studies of Ferroelectric [NH<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>]<sub>3</sub>Sb<sub>2</sub>Cl<sub>9</sub> Crystals under Moderate Pressure

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The effect of pressure on the dielectric properties of [NH<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>]<sub>3</sub>Sb<sub>2</sub>Cl<sub>9</sub> crystal was analyzed for a few values of hydrostatic pressure within the range from 0.1 MPa to 300 MPa and for temperatures from the range of 220–350 K. The measuring frequency was 1 kHz. The pressure–temperature phase diagram obtained was nonlinear. The temperature dielectric permittivity anomalies related to the paraelectric-ferroelectric phase transition temperature ( $T_c$ ) gradually increase up to 66 MPa and then decrease with subsequent increase in pressure. The character of the temperature dielectric permittivity anomalies, typical of the continuous ferroelectric transition, remains unchanged with increasing pressure. Additionally, the pressure dependences of the Curie–Weiss constants for the crystal in paraelectric ( $C_+$ ) and ferroelectric ( $C_-$ ) phases were evaluated and discussed. The results indicated a complex mechanism of the ferroelectric phase transition.

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## 1. Introduction

Ferroelectric Tris (dimethylammonium) nanochloroantimonate — [NH<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>]<sub>3</sub>Sb<sub>2</sub>Cl<sub>9</sub> (abbreviated as DMACA) belongs to a family of organic-inorganic crystals of the general formula [NH<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>]<sub>3</sub>M<sub>2</sub>X<sub>9</sub> (M stands for

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metal (III): Sb, and X stands for halogen atoms: Cl, Br, I) [1]. The X-ray investigation [2] has shown that at room temperature the DMACA crystal is of monoclinic symmetry (space group  $P2_1/c$ , point group  $2/m$ ). The crystal structure is formed by rigid two-dimensional layers of  $[\text{Sb}_2\text{Cl}_9^{3-}]_n$  polyanions with large vacancies and two types of crystallographic non-equivalent disordered dimethylammonium cations (DMA(1) and DMA(2)). The cations form relatively weak hydrogen bonds of the N–H...Cl type with anionic halogen atoms (Fig. 1). The DMA(1) cations (placed inside the twelve-membered  $(-\text{Sb}-\text{Cl})_6$  rings of the anionic layers) are distributed between two positions with the same probability ( $180^\circ$  reorientation), while the cations DMA(2) are located in the general position between the layers [2].

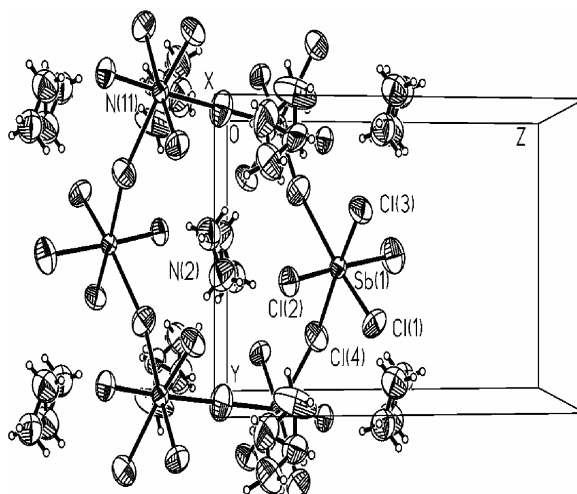


Fig. 1. The projection of the crystal structure of DMACA in the  $a$  direction at 293 K.

At 242 K the DMACA crystal undergoes continuous ferroelectric phase transition from  $P2_1/c$  to  $Pc$  [3]. It is known from literature [1] that for halogenoantimonates (III) and halogenobismuthates (III) of  $\text{R}_3\text{M}_2\text{X}_9$  composition, the origin of ferroelectricity is undoubtedly related to the presence of two-dimensional anionic layers. Therefore, it can be expected that the long-range dipole–dipole interactions (leading to the ferroelectric ordering) depend on the coupling between the cationic (organic) and anionic sublattices.

On the basis of the X-ray [2, 3] dielectric dispersion [4] and NMR [5] studies DMACA was classified as one of the most typical ferroelectrics showing the order-disorder phase transition, where DMA cations are treated as the order-disorder unit. However, the IR and Raman spectroscopic studies have indicated the importance of N–H...Cl hydrogen bonds contribution to the mechanism of the ferroelectric phase transition [6–8]. It is supposed that important additional information, especially that concerning the nature of the phase transition, should

be obtained from the detailed dielectric studies under high hydrostatic pressure. In the present paper we report the effect of pressure on the ferroelectric properties of  $[\text{NH}_2(\text{CH}_3)_2]_3\text{Sb}_2\text{Cl}_9$  crystal up to 300 MPa. The possible mechanism of paraelectric-ferroelectric phase transition is also discussed.

## 2. Experimental

The method of single crystal preparation of  $[\text{NH}_2(\text{CH}_3)_2]_3\text{Sb}_2\text{Cl}_9$  was described earlier [2]. The crystals used for the dielectric measurements were cut perpendicular to the  $c$ -axis, covered with silver paste, and placed between two parallel silver plates. The dielectric properties of  $[\text{NH}_2(\text{CH}_3)_2]_3\text{Sb}_2\text{Cl}_9$  were measured by an automatic capacitance bridge meter Hewlett-Packard HP 4270A at the frequencies: 1 kHz, 10 kHz, 100 kHz, and 1 MHz, at a few values of hydrostatic pressure within the range from 0.1 MPa to 300 MPa and within the temperature range of 220–350 K. The measuring ac electric field was about 1 V/cm.

The high pressures were generated by means of IF-012 A Unipress helium gas compressor. Pressure was measured to an accuracy of 0.2 MPa by means of a manganine gauge (previously calibrated by reference to the pressure-induced phase transition of bismuth) with a Keithley 2400 Source Meter. The pressure chamber (made of beryllium–copper alloy) was placed into an Oxford flow cryostat. The temperature of the sample was set and stabilized using an Oxford Instruments automatic temperature controller ITC4. The temperature was measured to an accuracy of 0.1 K by means of a Pt 100 sensor located inside the pressure chamber. Measurements were performed on heating and on cooling. The heating/cooling rate in the vicinity of the phase transition was 0.05 K/min. Data collections were made using LabApp program working on Aurox-Linux platform.

## 3. Results

Figure 1 shows the temperature dependences of the real part of the complex electric permittivity ( $\epsilon'_c$ ) of DMACA measured along the ferroelectric direction in different isobaric conditions. For simplicity, only measurements performed at 1 kHz are presented. The maximum of the dielectric permittivity value corresponding to the paraelectric-ferroelectric phase transition ( $T_c$ ) increases with increasing pressure up to 66 MPa and its position is shifted towards higher temperatures. Above 66 MPa, the maximum of the electric permittivity ( $\epsilon'$ ) gradually decreases with increasing pressure and its position is considerably shifted towards lower temperatures. The character of the temperature dielectric permittivity anomalies, typical of the continuous ferroelectric transition, remains unchanged with pressure increasing up to 300 MPa.

The pressure–temperature phase diagram of DMACA is presented in Fig. 2. The phase transition temperature  $T_c$  for each pressure is defined as the temperature at which  $\epsilon'$  attains a maximum. The relation between  $T_c$  and pressure  $p$  is not linear over the studied pressure region. The low pressure region (up to 66 MPa) is

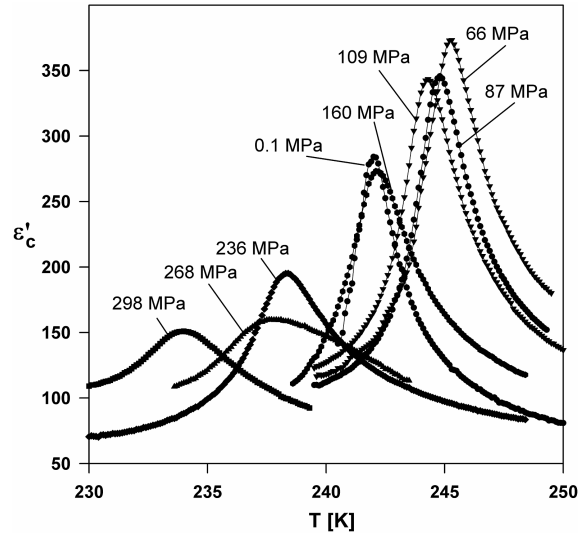


Fig. 2. The real part of the complex electric permittivity ( $\varepsilon'_c$ ) of DMACA as a function of temperature at eight constant values of pressure; measured frequency is 1 kHz (on heating).

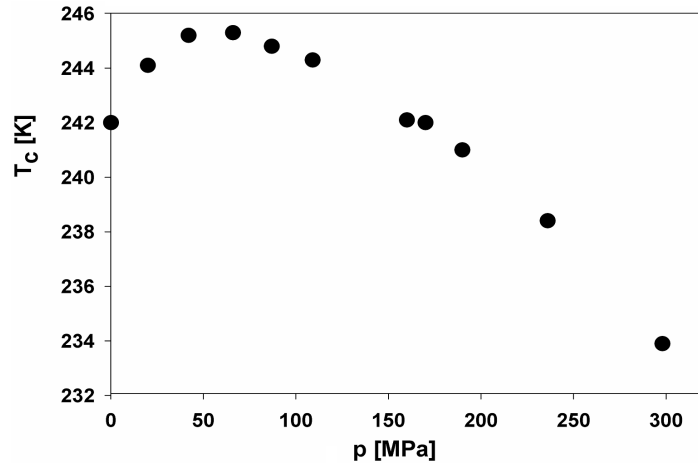


Fig. 3. The pressure–temperature phase diagram of DMACA.

characterized by the positive pressure coefficient  $dT_c/dp$ , whereas above 66 MPa the phase transition temperature decreases with increasing pressure.

The temperature dependences of the reciprocal relative permittivity ( $1/\varepsilon'$ ) for different isobaric conditions (measured at 1 kHz) presented in Fig. 3 indicate that the Curie–Weiss law is well obeyed both in the paraelectric (PE) and ferroelectric (FE) phases.

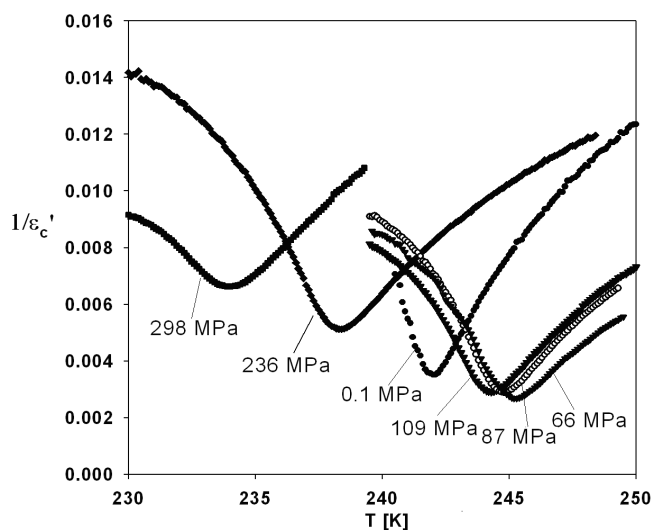


Fig. 4. The temperature dependences of the reciprocal relative permittivity of the DMACA crystal for different isobaric conditions at the frequency 1 kHz (on heating).

The Curie constants were evaluated (for each value of pressure applied) from dielectric permittivity anomalies by fitting  $\epsilon'$  to the Curie–Weiss law:  $\epsilon' = \epsilon_\infty + C^{(p)}/(T - T_c^{(p)})$ , where  $C^{(p)}$  is the Curie constant and  $T_c^{(p)}$  is the phase transition temperature. The introduced superscript ( $p$ ) emphasizes that  $C$  and  $T_c$  are functions of pressure. The results are presented in Fig. 4. The magnitude of the Curie constants is of the order of  $10^3$  and the ratio  $C_+/C_-$  is near 2 at ambient pressure. The data suggest that the phase transition in DMACA is of order-disorder type at ambient pressure. Both Curie constants  $C_-$  and  $C_+$  stay almost constant versus pressure even if  $T_c$  decreases.

#### 4. Discussion

Ferroelectric crystals are usually classified into two types: the order-disorder and displacive. It was pointed out by Onodera and Kojyo (in the ferroelectric phase transitions unified model) [9] that the order-disorder type ferroelectrics have well defined permanent dipoles, and even weak cooperative interactions between them lead to the ferroelectric state. The relation between  $T_c$  and the coupling constant  $J$  for the order-disorder type ferroelectrics (in the molecular field approximation) is  $kT_c = \mu_c^2 J$ . The parameter  $J$  is proportional to  $r^{-3}$  ( $r$  denotes the distance between two dipoles). Under elevated pressure the distances between ions decrease, therefore, the parameter  $J$  as well as the phase transition temperature  $T_c$  are expected to increase. Additionally, the hydrostatic pressure affects the configuration of the hydrogen bonds (their lengths and angles) [10] leading to drastic changes in the shape of the cations movement potential and (in consequence) to ordering of the cations. As shown by the X-ray low temperature data for DMACA [3] a

relatively small displacement of the N atoms, of the order of  $0.10 \div 0.15 \text{ \AA}$ , with respect to the anionic sublattice in the ferroelectric phase, is sufficient to considerably diminish the  $180^\circ$  reorientation of DMA cations placed within the anionic layers. Therefore, up to 66 MPa, the value of the  $dT_c/dp$  coefficient is positive in DMACA which is typical of pure order-disorder mechanism of the phase transition [11]. The above conclusion is consistent with the Samara classification of ferroelectrics [11] as well as with the earlier results of the dielectric [1, 4], X-ray [2, 3], Raman and IR studies [6–8] of DMACA.

Above 66 MPa the ferroelectric phase transition temperature decreases with increasing pressure. The effect observed is probably a result of a competition between the structural features related to the hydrogen bonds, i.e. the deformation of the N–H...Cl angles and changes in the N...Cl distances and van der Waals and electrostatic interactions. At elevated pressures the molecules (ions) become more tightly packed and their intermolecular van der Waals and electrostatic interactions with the environment increase, favoring more symmetric arrangements [12, 13]. The sign of the pressure coefficient  $dT_c/dp$  depends on the interaction type that dominates under high pressure conditions in DMACA.

An interesting point is the pressure effect on the Curie constants as shown in Fig. 5. The magnitude of the Curie constant  $C$  ( $10^3$ ) and the ratio  $C_+/C_-$  (near 2) at ambient pressure suggest that the phase transition in DMACA is of order-disorder type. Our pressure results (similar to those obtained by Endo *et al.* [14–16] in KDP-like ferroelectrics) have shown that  $T_c$  decreases vs. pressure and the Curie constants  $C_+$  (over the paraelectric phase) and  $C_-$  (over the ferroelectric phase) stay unchanged. In other words the relation  $C \sim (\varepsilon_\infty + 2)T_c$  (obeyed in most order-disorder type of ferroelectrics) no longer holds. Endo has shown within the phenomenological theory of phase transitions that the vanishing ferroelectric phase and constant  $C_+$  under high pressure in KDP-like ferroelectrics are related to the crossover to the displacive type of the phase transition mechanism [14, 16]. According to Endo conclusions, one can say that under moderate pressure applied in our experiment the phase transition mechanism in DMACA turns into the displacive one.

On the other hand, the magnitude of the Curie constant and the  $C_+/C_-$  ratio for DMACA, both stay unchanged at different isobaric conditions which suggests that the phase transition type does not change.

The above results can be explained in the following way. The paraelectric dipole moments  $\mu_c$  in ferroelectric crystals are defined through the Curie constant by the following relation:  $C_+ = 4\pi n\mu_c^2/k_B$ , where  $n$  denotes the number density of dipoles. The constant  $C_+$  remaining unchanged versus pressure indicates that the range of high pressure applied in our experiment is too small to generate significant changes in the dipole moment of the system. The applied pressure shortens the distances between interacting dipoles. It probably leads to the strengthening of local coupling between them. In other words both local short range interactions

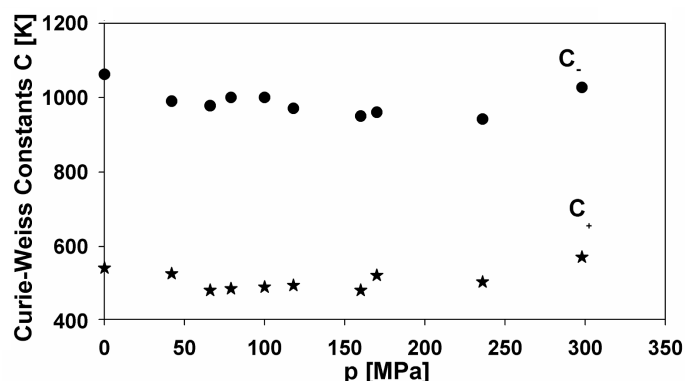


Fig. 5. The pressure dependence of the Curie–Weiss constants  $C_+$  (over the paraelectric phase) and  $C_-$  (over the ferroelectric phase) of the DMACA crystal.

and local order stand more important than the long-range ones. In consequence, the ferroelectric phase becomes unstable, which leads to the phase transition temperature decrease.

To draw reliable conclusions on the mechanism of the ferroelectric phase transition in the DMACA crystal, further pieces of information are needed to be obtained by the NMR and dielectric methods under higher pressure.

## 5. Conclusion

— The data presented above have shown that the phase transition in DMACA is of the order-disorder type with DMA cations rotational disorder in the high temperature phase but the stability of ferroelectric phase depends on the coupling with the anionic sublattice via the hydrogen bond network.

— The increase in the local order importance in comparison with the long-range one probably results in the ferroelectric phase instability. This hypothesis is consistent with the results of X-ray [2, 3], dielectric [1, 4], and  $^1\text{H}$  NMR [5] relaxation measurements.

## References

- [1] R. Jakubas, L. Sobczyk, *Phase Transit.* **20**, 163 (1990).
- [2] M. Gdaniec, Z. Kosturkiewicz, R. Jakubas, L. Sobczyk, *Ferroelectrics* **77**, 31 (1988).
- [3] J. Zaleski, A. Pietraszko, *Acta Crystallogr. B* **52**, 287 (1996).
- [4] G. Bator, R. Jakubas, *Phys. Status Solidi A* **147**, 591 (1995).
- [5] B. Jagadeesh, P.K. Rajan, K. Venu, V.S.S. Sastry, *Solid State Commun.* **91**, 843 (1994).
- [6] V. Varma, R. Bhattacharjee, H.N. Vasan, C.N.R. Rao, *Spectrochim. Acta A* **48**, 1631 (1992).
- [7] R. Jakubas, Z. Malarski, L. Sobczyk, *Ferroelectrics* **80**, 193 (1988).

- [8] G. Bator, R. Jakubas, J. Lefebvre, Y. Guinet, *Vibrat. Spectrosc.* **18**, 203 (1998).
- [9] Y. Onodera, N. Kojyo, *J. Phys. Soc. Jpn.* **58**, 3227 (1989).
- [10] *The Hydrogen Bond. Structure and Spectroscopy*, Eds. P. Schuster, G. Zundel, G. Sandorfy, North Holland, Amsterdam 1976.
- [11] G.A. Samara, T. Sakudo, K. Yoshimitsu, *Phys. Rev. Lett.* **35**, 1767 (1975).
- [12] A. Katrusiak, *Phys. Rev. B* **48**, 2992 (1993).
- [13] A. Katrusiak, *J. Mol. Struct.* **374**, 177 (1996).
- [14] S. Endo, T. Sawada, T. Tsukawake, Y. Kobayashi, M. Ishizuka, K. Deguchi, M. Tokunaga, *Solid State Commun.* **112**, 655 (1999).
- [15] S. Endo, K. Deguchi, *J. Phys., Condens. Matter* **14**, 11139 (2002).
- [16] S. Endo, K. Deguchi, M. Tokunaga, *J. Phys., Condens. Matter* **14**, 11275 (2002).