The influence of hydrostatic pressure on the ferroelectric phase transition in $(C_3N_2H_5)_5Bi_2Cl_{11}$

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Abstract

Single crystals of pentakis (imidazolium) undecachlorodibismuthate (III); $(C_3N_2H_5)_5Bi_2Cl_{11}$, have been studied by the dielectric method at ambient and hydrostatic pressures. At ambient pressure the crystals undergo a ferroelectric phase transition of order–disorder type at 166 K. The character of the dielectric permittivity anomalies is typical of the ferroelectric phase transition close to second-order type. The magnitude of the Curie constants of paraelectric (C_+) and ferroelectric (C_-) phases is of the order of 10^3 and the $(C_+)/(C_-)$ ratio is near 2. At elevated pressures the maximum dielectric permittivity corresponding to the (T_c) value gradually decreases with increasing pressure. In addition, above about 15 MPa the dielectric permittivity shows a step-like behaviour as well as a temperature hysteresis, which is typical of first-order phase transitions. The Curie–Weiss constant (C_+) rapidly increases with increasing pressure, reaching a value of the order of 10^5 at about 181 MPa. The pressure-induced change in the phase transition type is continuous and reversible. The phase boundary has been found to decrease nonlinearly with increasing pressure with the initial slope of $dT_c/dp = -3.9 \times 10^{-2}$ K MPa^{-1}. The results have been discussed within the phenomenological model of phase transitions.

1. Introduction

Halogenoantimonates (III) and halogenobismuthates (III) described by the general formula $R_a M_b X_{(3b+a)}$ where R denotes organic cations, M denotes Sb(III) and Bi(III) atoms and X stands Cl, Br and I, have been found to exhibit interesting ferroic (ferroelectric/ferroelastic) properties [1, 2]. From among these compounds, in the salts crystallizing with the chemical composition $R_3M_2X_9$ and $R_5M_2X_{11}$ [3–7] ferroelectricity has been found to appear. For the former subgroup of salts, which may adopt four different anionic structures, the ferroelectricity appears only in the derivatives possessing two-dimensional anionic layers, $(M_2X_9{}^{3-})_\infty$ [8, 9]. In contrast, the second subgroup is characterized by discrete bi-octahedral units $Bi_2X_{11}{}^{5-}$ and, so far, only four examples of salt crystallizing with this chemical composition have been synthesized, and all of them have ferroelectric

properties [14–16]. The $R_5M_2X_{11}$ type crystals appeared to be more attractive, from the application point of view, because their methylammonium analogues have dielectric properties comparable to those found for the well known TGS (triglycinium sulfate) family of ferroelectric crystals [12]. The methylammonium compounds, $(CH_3NH_3)_5Bi_2Cl_{11}$ (MAPCB) and $(CH_3NH_3)_5Bi_2Br_{11}$ (MAPBB), undergo paraelectric–ferroelectric phase transitions at 307 and 311 K, respectively. The ferroelectric phase transition is accompanied by a relatively large dielectric permittivity of the order of 10^4 units and the saturated spontaneous polarization reaches a value 3×10^{-2} C m^{-2} [10, 11]. The transition was expected to be promoted by an order–disorder process of $CH_3NH_3{}^+$ ions. This model of the ferroelectric phase transition mechanism was confirmed by observation of the critical slowing down [10] as well as via results of high pressure studies [13–15]. For both methylammonium compounds the character of the

dielectric permittivity anomalies, typical of the continuous ferroelectric transition, remains unchanged with increasing pressure. The Curie temperatures nonlinearly increase with increasing pressure with the initial pressure coefficients of $dT_c/dp = 0.063$ K MPa^{-1} and 0.060 K MPa^{-1} for MAPCB and MAPBB, respectively. The authors have suggested that the marked nonlinear p, T diagram obtained for both MAPCB and MAPBB crystals can be related to a crossover of the ferroelectric phase transition mechanism from order–disorder type to a displacive one. Until now, there has been no experimental evidence confirming the above conclusions.

Recently, we have extended our studies to the compounds comprising pentagonal aromatic cations in their crystal structure. The $R_5M_2X_{11}$ analogues containing aromatic cations like pyridinium and imidazolium—$(C_5H_5NH)_5Bi_2Br_{11}$ and $(C_3H_5N_2)_5Bi_2Cl_{11}$—reveal ferroelectric properties at significantly lower temperatures in comparison to those reported for methylammonium analogues [16–18]. Despite the structural similarities of all the $R_5M_2X_{11}$ type compounds, the physical properties of methylammonium analogues and aromatic ones differ significantly. Their dielectric constants at T_c and spontaneous polarizations are distinctly smaller in comparison to those found for the methylammonium analogues.

The title crystal, $(C_3H_5N_2)_5Bi_2Cl_{11}$ (ICB), exhibits the following sequence of phase transitions:

$$P\bar{4}n2 \xrightarrow{360\ K} P2_1/n(\mathrm{I} \to \mathrm{II}),\ P2_1/n \xrightarrow{166\ K} P2_1(\mathrm{II} \to \mathrm{III}).$$
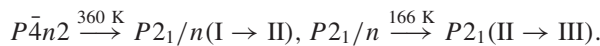
The high temperature phase transition leads from the paraelastic phase (tetragonal symmetry) to the ferroelastic/paraelectric one (monoclinic). The lower temperature phase transition at 166 K leads to the ferroelectric order. The phase transition mechanism at 166 K of an order–disorder type is postulated to be governed by the dynamics of imidazolium cations. Recently, the ferroelectric phase transition observed in IBC has been described using the Landau model, using specific heat data [19]. The authors of [19] have fully confirmed the two-site model, describing the motion of three of the five imidazolium cations in $(C_3H_5N_2)_5Bi_2Cl_{11}$ at ambient pressure. The ac calorimetry study of ICB led to an interesting conclusion: that the ferroelectric transition shows features of both of first- and second-order type. Thus, the tricritical point postulated on the basis of the above study should be located not far ($\sim$0.06 K) from T_C at ambient pressure. Such a behaviour suggests that the crystal of ICB under an external driving force may change the character of the transition from the second-order to first-order one. The pressure studies, in this case, are expected to make a significant contribution to the understanding of the nature of the ferroelectric phenomena involved.

The purpose of this work is to examine the ferroelectric properties of the ICB crystal under an external hydrostatic pressure. The study also aims to induce by means of pressure a critical end-point for the ICB crystal as well as to induce a phase transition type change from the second-order to first-order one, as predicted by Przesławski *et al* [19] on the basis of ac calorimetric studies. A possible mechanism of the paraelectric–ferroelectric phase transition is also discussed.

2. Experimental details

The method of single-crystal preparation of $(C_3N_2H_5)_5Bi_2Cl_{11}$ was described earlier [17]. The dielectric properties of $(C_3N_2H_5)_5Bi_2Cl_{11}$ were measured using an impedance analyser, Hewlett-Packard HP 4284A, for the frequencies from 100 Hz to 1 MHz for the selected values of the hydrostatic pressure within the range from 0.1 to 300 MPa and within the temperature range from 77 to 180 K. The measuring ac electric field was about 1 V cm^{-1}. The measurements were performed along the axis placed within the *ac* plane of the monoclinic system (direction [401]) for the $(C_3N_2H_5)_5Bi_2Cl_{11}$ crystal. The crystals used for the dielectric measurements were covered with carbon paste and placed between two parallel gold plates. High pressures were generated by means of an IF-012 A Unipress helium gas compressor. Pressure was measured to an accuracy of 0.2 MPa by means of a manganin 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 in an Oxford flow cryostat. The temperature of the sample was set and stabilized using the Oxford Instruments automatic temperature controller ITC4. The temperature was measured with an accuracy to 0.01 K by means of a Pt100 sensor located inside the pressure chamber. Measurements were performed on heating and cooling. The heating/cooling rate in the vicinity of the phase transition was 0.02 K min^{-1}.

Data collections were done using an Agilent Vee Pro 7.0 program.

3. Results

Figure 1 shows the temperature dependences of the real part of the complex dielectric permittivity (ε') of ICB measured along the direction [401] for different isobaric conditions. The measurements were performed for the same sample of ICB at 200 Hz. It should be noted that in our experiment the ferroelectric transition at ambient pressure takes place at about 162 K, whereas the previous studies reported the transition temperatures of 165 K [19] and 166 K [17]. This discrepancy may be due to the fact that the pressure measurements were made in the static regime (stabilization of temperature), whereas the dielectric and calorimetric studies were carried out in the dynamical regime.

At ambient pressure the static dielectric response (see figure 1) shows behaviour close to typical for the second-order type phase transition. The transition to the ferroelectric phase was observed on heating and cooling the sample with a hysteresis of about 0.3 K at ambient pressure. This experimental fact also suggests that the phase transition of ICB at ambient pressure is not the pure second-order one. Above about 15 MPa the anomaly of dielectric permittivity shows a step-like behaviour (see figure 2 for example), which is characteristic of a first-order (discontinuous) phase transition. The temperature hysteresis increases at elevated pressures. The maximum of the dielectric permittivity value corresponding to the paraelectric–ferroelectric phase transition (T_c) decreases
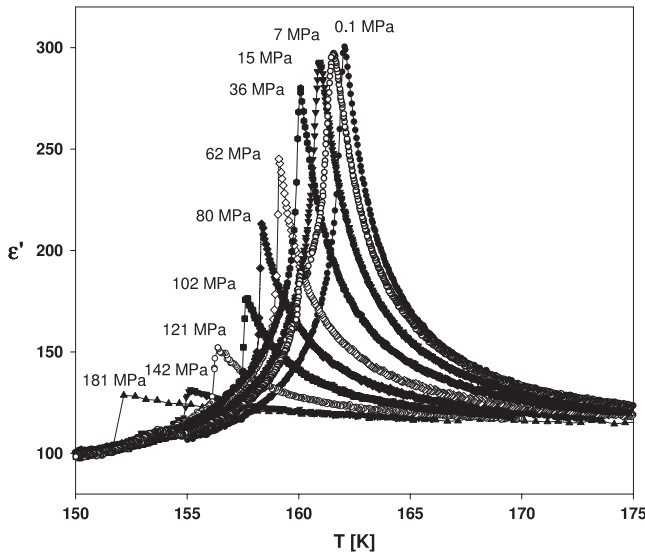
Figure 1. The real part of the complex electric permittivity of ICB (ε') as a function of temperature under different constant values of pressure; at the measuring frequency of 200 Hz (on cooling, measured along direction [401]).
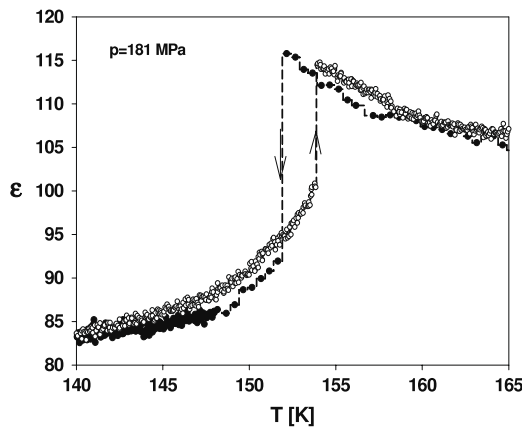

Figure 2. Temperature dependence of (ε') measured along direction [401] under isobaric conditions on cooling and heating; at the measuring frequency of 200 Hz, $p = 181$ MPa.

with increasing pressure and its position is considerably shifted towards lower temperatures.

An interesting feature observed for ICB is a continuous and reversible change of the phase transition character. Recently, a phase transition observed in IBC has been described using the Landau model, using specific heat data [19]. The authors of [19] have fully confirmed the two-site model describing the motion of three of the five imidazolium cations in $(C_3H_5N_2)_5Bi_2Cl_{11}$ at ambient pressure. Additionally, the ac calorimetry study of ICB also leads to interesting results. It has been shown that in the title crystal the paraelectric–ferroelectric transition is rather close to the tricritical one. The expected tricritical point should be located not far ($\sim$0.06 K) from T_c. Such a behaviour suggests that our crystal under an external driving force may change the character of the transition from the second-order to first-order
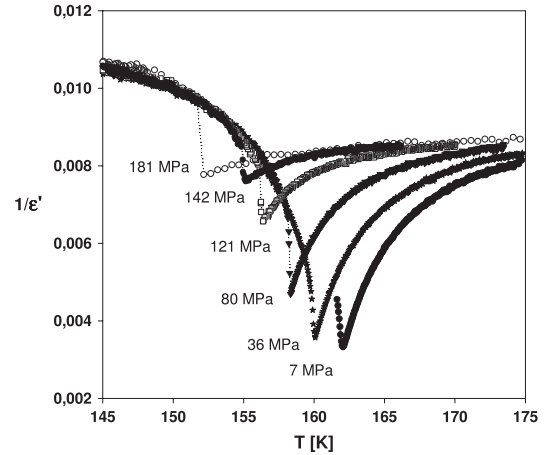

Figure 3. The temperature dependences of the reciprocal relative permittivity ($1/\varepsilon'$) for selected pressures in ICB; at the measuring frequency of 200 Hz (on cooling).

one. Our pressure results provide an excellent illustration and support for the ac calorimetric studies reported by Przesławski *et al* [19].

The dielectric manifestation of the tricritical point can be deduced on the basis of Landau theory of phase transitions [20]. Going from the second-order transition regime to a tricritical point, the slope ratio for the $(\varepsilon')^{-1}$ versus $(T - T_c)$ dependence, going from that below T_c to that above T_c, should change from 2 to 4 at the phase boundary. It was found from our pressure experiment that for ICB the tricritical point corresponds to $T_t \sim 160.08$ K and $p \sim 15$ MPa. The fitting procedure has been performed for the same temperature interval limited to 1.5 K for the low and high temperature phases.

The temperature dependences of the reciprocal relative permittivity $1/\varepsilon'$ for different pressures at 200 Hz in ICB are shown in figure 3. As follows, the Curie–Weiss law ($\varepsilon' = \varepsilon_\infty + C^{(p)}/(T - T_c^{(p)})$, where $C^{(p)}$ is constant and $T_c^{(p)}$ is the phase transition temperature) is not well obeyed. Linear dependence of $1/\varepsilon'$ is observed only within a narrow temperature region of about 1.5 K, both above and below the Curie temperature. Both magnitudes, C_+ (in the paraelectric phase) and C_- (in the ferroelectric phase) depend strongly on the frequency of the measuring electric field.

On the basis of the temperature dependences of the reciprocal relative permittivity $1/\varepsilon'$ for different isobaric conditions, given in figure 3, the Curie constants C_+ are evaluated by fitting ε' to the Curie–Weiss law and the pressure effect on the Curie constants C_+ is examined (figure 4). In the fitting procedure, the temperature interval ($T - T_c \sim 1.5$ K). has been taken into account for each pressure applied in our experiment. The magnitude of the Curie constants C (10^3) at ambient pressure suggests that the ferroelectric phase transition in ICB is of the order–disorder type. The above conclusion is consistent with the earlier results of the dielectric [17, 18], x-ray [17] and ac calorimetry [19] studies on the ICB crystals. Above 40 MPa, the Curie constant rapidly increases versus pressure and attains a value of $\sim$10^5 K at 181 MPa. The order
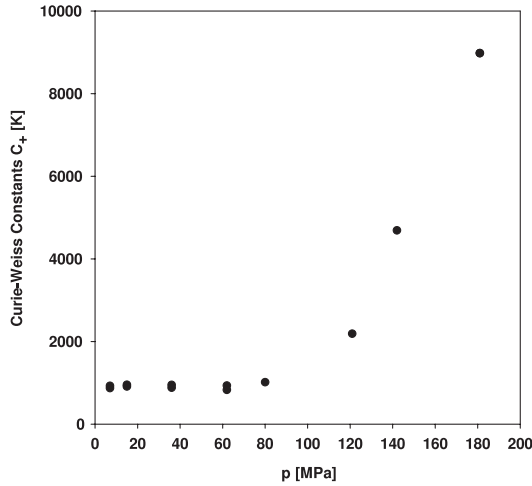
Figure 4. The pressure dependence of the Curie–Weiss constants $C_{(+)}$ for ICB in the paraelectric phase.

Figure 5. The pressure dependence of the Curie–Weiss constants $C_{(+)}$ for ICB in the paraelectric phase.

Figure 6. The pressure–temperature phase diagram of ICB. The circles are experimental results. The dashed line presents the initial slope.

of magnitude of the Curie–Weiss constant (10^5 K) and the decrease in phase transition temperature under the influence of external pressure are typical of ferroelectrics of displacive type [20].

The Curie–Weiss constant pressure dependence and change in the phase transition character in ferroelectrics of displacive type within the phenomenological theory of phase transitions were studied by Slivka [21]. The analysis carried out by Slivka indicated that the pressure dependence of the Curie–Weiss constant C as well as a nonlinear character of the p, T phase boundary (experimentally established for the displacive type ferroelectrics) may be explained by the temperature change in the electrostriction coefficients of a crystals in its p, T diagram. According to [21], the pressure dependence of the Curie–Weiss constant $C(p)$ in displacive ferroelectrics may have nonlinear character (in the general case) and may be given in the simple form

$$C(p) = C^{(0)}(1 + fp + zp^2). \qquad (1)$$

Or it can be given in the normalized form

$$(C(p) - C^{(0)})/C^{(0)} = fp + zp^2 \qquad (2)$$

in which p is the hydrostatic pressure, $C^{(0)}$ is the Curie–Weiss constant at ambient pressure, f and z are the coefficients directly related to the electrostriction coefficient and the quadratic electrostriction coefficient, respectively.

The result of application of equation (2) in characterization of the pressure dependence of the Curie–Weiss constant of ICB is illustrated in figure 5.

Experimental data (points) are presented in the normalized form $(C^{(p)} - C^{(0)})/C^{(0)}$. The solid line (fitting curve) is generated using formula (2). A complete agreement between the results measured and the fitting with equation (2) asserts its correctness in the characterization of the Slivka model when applied to ICB. This means that within the phenomenological theory of phase transitions, the pressure dependence of the Curie–Weiss constants can be explained by the temperature
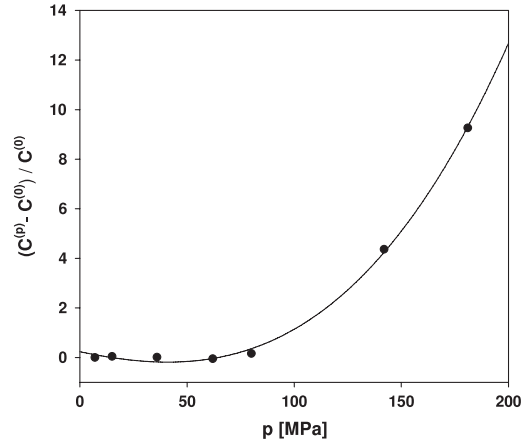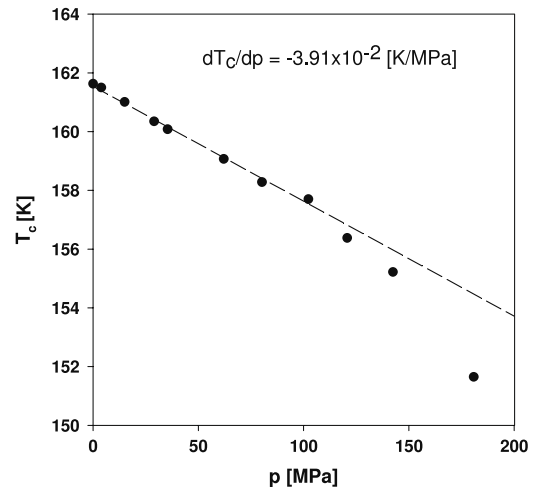
changes in the electrostriction coefficients of the crystal in its p, T diagram.

Figure 6 presents the ICB crystal pressure–temperature phase diagram. The phase transition temperature T_c for each pressure is defined as the temperature at which ε' attains a maximum. The relation between T_c and pressure p is not linear over the pressure region studied. The initial slope of the phase boundary (shown as a dashed line) is equal to -3.9×10^{-2} K MPa^{-1}.

Taking into consideration the phenomenological model of ferroelectrics of displacive type presented in [21], the pressure dependence of the phase transition temperature can be written in the following form:

$$T_c(p) = T_0 - (2g_0\varepsilon C^{(0)}/c)p - ((2g_0\varepsilon C^{(0)}/c)f$$
$$+ (h_0\varepsilon C^{(0)}/c^2))p^2 - ((2g_0\varepsilon C^{(0)}/c)z$$
$$+ (h_0\varepsilon C^{(0)}/c^2)f)p^3 \qquad (3)$$

in which f and z are the coefficients of the same meaning as in formula (1), c is the tensor of elastic modulus, g
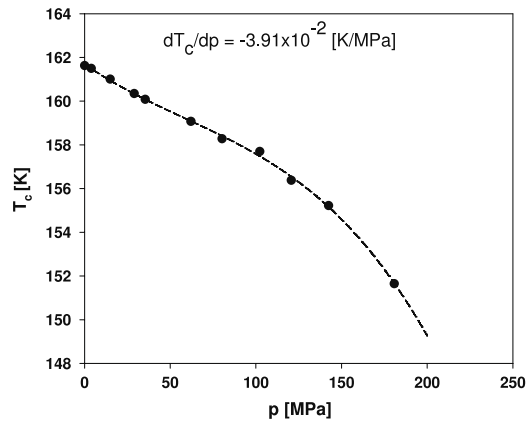
Figure 7. The pressure–temperature phase diagram of ICB. The circles are experimental results. The solid line is the fitting curve generated using formula (3).

is the electrostriction coefficient and h is the quadratic electrostriction coefficient.

The $T_c(p)$ dependence fitted with (3) is given in figure 7. Good agreement between the experimental results and the fitting curve indicates that the nonlinear characters of the temperature dependences of ferroelectric phase transition in ICB and the electrostriction coefficients are strictly related to each other.

4. Discussion

It seems interesting to compare the structural and dynamic properties of four ferroelectric compounds synthesized so far, which crystallize with the $R_5M_2X_{11}$ chemical composition. The methylammonium analogues undergo a paraelectric–ferroelectric transition within the orthorhombic symmetry: $Pcab \rightarrow Pca2_1$, at 311 $(CH_3NH_3)_5Bi_2Br_{11}$ and at 307 K $(CH_3NH_3)_5Bi_2Cl_{11}$. The two remaining compounds containing aromatic cations (pyridinium and imidazolium), $(C_5H_5NH)_5Bi_2Br_{11}$ and $(C_3H_5N_2)_5Bi_2Cl_{11}$, preserve the monoclinic symmetry over the ferroelectric phase transition, $P2_1/n \rightarrow P2_1$, at 118 and 166 K, respectively. Despite these obvious structural differences, the common features of all four compounds are the following experimental facts concerning the paraelectric–ferroelectric transitions at ambient pressure:

- The nature of the ferroelectric transitions is clearly continuous.
- The transitions are classified as the order–disorder type.
- The molecular mechanism of the ferroelectric transition is believed to be governed by the dynamics of the organic cations. In the paraelectric phase two of the five cations placed in the general positions are ordered and do not contribute to the ferroelectric properties. The remaining three cations (placed in special positions) are disordered and distributed over two sites. In the ferroelectric phase they become ordered (continuously with temperature) and when the spontaneous polarization reaches its saturated magnitude they are fully ordered.

The most striking feature which differentiates the methylammonium and aromatic analogues is a substantial shift of the Curie temperature and reduction of the dielectric constants (ε') at T_c and the spontaneous polarization (P_s) magnitude. In the aromatic analogues both ε' and P_s are nearly one order smaller in magnitude than those found for the methylammonium ones. This means that the interactions which lead to a long range ferroelectric order are significantly stronger in the methylammonium analogues.

The second important feature which distinguishes between methylammonium and aromatic derivatives is the sign of the pressure coefficient (dT_c/dp) obtained on the basis of the pressure studies. Taking into account all the structural arguments, we could expect a similar influence of the hydrostatic pressure on stabilization of the ferroelectric phases. The methylammonium derivatives are characterized by positive pressure coefficients for the ferroelectric transitions, but unexpectedly, the title crystal reveals clearly a negative one. This is the most important qualitative difference for the analysed crystals. The question arises of what the microscopic reason for such a behaviour is.

In interpretation of pressure results for the ICB crystal we have used the phenomenological model proposed by Slivka [21]. According to this model, the nonlinear decrease in T_c with pressure, the pressure dependence of the Curie Weiss constant C and the appearance of the polycritical points in the phase diagrams can be explained by the temperature changes in the electrostriction coefficients. Excellent agreement between the experimental results and the fitting curves, seen in figures 4(b) and 5(b), indicates that the ferroelectric properties of ICB are strictly related to the electrostriction effect.

Our experimental results and their interpretation indicate that a general approach assuming that the ferroelectric phase stability and the type of phase transition are a direct result of the competition between short and long range dipole–dipole interactions does not always hold. It seems important to consider other features which commonly occur in the ferroelectric compounds like the piezoelectric and electrostriction effects.

5. Conclusion

The hydrostatic pressure effect on ferroelectric properties of the $(C_3H_5N_2)_5Bi_2Cl_{11}$ (ICB) crystal has been studied by means of dielectric permittivity measurements over a wide range of temperatures. It is apparent from our studies that a relatively low hydrostatic pressure induces a crossover from order–disorder to displacive type in the ferroelectric phase transition mechanism. This experimental fact confirms the thermodynamic instability of the title compound predicted on the basis of the ac calorimetric studies [19].

The experimental data analysis indicates that within the phenomenological theory of phase transitions the pressure dependence of the Curie constant C_+ as well as the pressure dependence of the phase transition temperature T_c can be explained by the temperature changes in the electrostriction coefficients of the crystal studied in its phase p, T diagram.

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