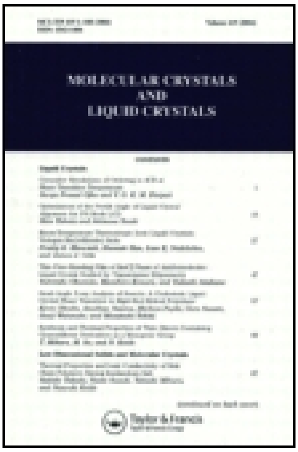

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Spontaneous Polarization and Dielectric Properties of Methylammonium Halogenobismuthate Crystals Under Hydrostatic Pressure

R. Poprawski [a] & W. Salejda [a]

[a] Institute of Physics, Technical University of Wroclaw, 50-370, Wroclaw, Wybrzeże Wyspia[ngrave]skiego 27, Poland

To cite this article: R. Poprawski & W. Salejda (1993): Spontaneous Polarization and Dielectric Properties of Methylammonium Halogenobismuthate Crystals Under Hydrostatic Pressure, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 229:1, 215-220

To link to this article: http://dx.doi.org/10.1080/10587259308032199

Mol. Cryst. Liq. Cryst. 1993, Vol. 229, pp. 215–220
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

SPONTANEOUS POLARIZATION AND DIELECTRIC PROPERTIES OF METHYLAMMONIUM HALOGENOBISMUTHATE CRYSTALS UNDER HYDROSTATIC PRESSURE

R. Poprawski and W. Salejda
Institute of Physics, Technical University of Wroclaw, 50-370 Wroclaw,
Wybrzeże Wyspiańskiego 27, Poland

Abstract Within a phenomenological approach we have interpreted the experimental dependence of dielectric properties of $(CH_3NH_3)_5Bi_2Br_{11}$ (MAPBB) and $(CH_2NH_3)_5Bi_2Cl_{11}$ (MAPCB) under hydrostatic pressure. We have shown that the thermodynamic state of the crystals is determined by: (1) $\Delta T = T - T_c(p)$ at $p = const$; (2) $\Delta p = p - p_c(T)$ at $T = const$, where $T_c(p)$ $(p_c(T))$ denotes the Curie temperature (the Curie pressure) depending on pressure (temperature). This means that the hydrostatic pressure plays the same role as the temperature. In order to describe the pressure dependence of the spontaneous polarization the pressureelectric effect (PEE) has been introduced. Applicability of PEE to detection of pressure changes and direct conversion of elastic to electric energy is discussed.

INTRODUCTION

In $(CH_3NH_3)_5Bi_2Br_{11}$ (MAPBB) and $(CH_2NH_3)_5Bi_2Cl_{11}$ (MAPCB) crystals the second order ferroelectric phase transitions (PT) occur at $311K$, and $307K$, respectively[1,2]. The structural[3] and spectroscopic[4] investigations confirme the order-disorder character of the phase transitions in these crystals. The ordered molecules are methylammonium anions. These PT are typical examples of the "classical" order-disorder phase transitions (it means that in these crystals tunneling effect does not exist). According to Samara's[5] classification in the crystals of this type the positive shift of the phase transition temperature with the hydrostatic pressure (HP) is observed. This conclusion is confirmed by our experimental results[6,7]. The pressure coefficients of the phase transitions temperature shift dT_c/dp are $58K/GPa$ and $38K/GPa$ for MAPBB and MAPCB crystals respectively.

It is worth noticing that HP applied to ferroelectric crystals shows an effect on many physical properties and reveals a new phenomenon. One of the aims of this work is to describe phenomenologically an influence of the HP on physical properties of the crystals exhibiting the second-order ferroelectric phase transition. The conclusions drawn on the basis of the thermodynamic analysis are compared with the experimental results obtained for MAPBB and MAPCB crystals.

Pressureelectric effect consists in the hydrostatic-pressure-inducted generation of the free electric charge on the surface of polar crystals. The relation between the spontaneous polarization and hydrostatic pressure can be described with the help of pressure electric coefficients (PEC), η defined as a temperature derivative over the spontaneous polarization ($\eta = dP_s/dp$). The PEE can be applied to the direct conversion from the elastic to the electric energy. The presentation of the physical principles of the pressure electric convectors and sensors is the other aim of this work.

PHENOMENOLOGICAL MODEL

Experimental investigations[8,9] confirm that the relation between dielectric permittivity, ϵ and temperature T for ferroelectrics showing the second order PT can be described by the Curie-Weiss law

$$\epsilon = \frac{C}{T - T_c} \tag{1}$$

where T_c is the phase transition temperature. This temperature is a function of the HP

$$T_c = T_{co} + \int_o^p \frac{\partial T_c}{\partial p}\, dp \tag{2}$$

where T_{co} denotes the phase transition temperature under normal pressure, p – pressure. If we assume that $\Omega = \partial T/\partial p = const.$ the relation (2) can be rewritten in the form

$$T_c = T_{co} + \Omega \cdot p \tag{3}$$

Coefficient Ω can be positive or negative. According to Samara's[5] classification $\Omega > 0$ for the crystals exhibiting classical order-disorder phase transitions and $\Omega < 0$ for hydrogen-bound crystals.

Pressure dependence of the dielectric permittivity satisfies the relation similar to the Curie-Weiss rule

$$\epsilon = \frac{K}{p - p_c} \tag{4}$$

where p_c is the phase transition pressure.

Taking into acount the relations (1), (3) and (5) the Gibbs function for mechanical free uniaxial ferroelectric crystals can be written in the form

$$G = G_o + \frac{\alpha}{2}(T - T_c - \Omega \cdot p)P^2 + \frac{\beta}{4}P^4 - E \cdot P \tag{5}$$

where: P – polarization, E – electric field intensity, α, β – are coefficients of the Gibbs function expansion.

DIELECTRIC PROPERTIES

Minimizing the Gibbs function (5) with respect to the polarization P at E = 0 we obtain the relation between dielectric permittivity, temperature and pressure

$$\frac{1}{\kappa} \cong \frac{1}{\epsilon} = \alpha (T - T_{co} - \Omega \cdot p) \tag{6}$$

At constant pressure p (temperature T) the reverse dielectric permittivity is a linear function of the temperature T (hydrostatic pressure p). These relations are illustrated in the Fig.1. and Fig.2. showing the temperature and pressure dependence of the reverse dielectric permitivity for MAPBB and MAPCB crystals. The results were obtained from isotherms and isobars[6,7].

It is worth noticing that the term ($\Omega \cdot p$) in Eqs. (5) and (6) has a meaning of the phase transition temperature shift ΔT_c caused by the HP p. It is clearly seen from Eq.(5) that the thermodynamic state of the crystals is fully and unambiguously determined by the difference ΔT between temperature T and the phase transition temperature $T_c(p)$. In this sense the HP plays the same role as the temperature. On the basis of Eq.6 we can conclude that all results presented in Figs 1 and 2 may be represented using $T - T_c(p)$ variable only. Some examples of the relations between $1/\epsilon$ and $T - T_c$ obtained from isobars and isotherms for MAPBB and MAPCB crystals are shown in Fig.3 and Fig.4. We point out that the Curie constant obtained at different conditions (constant temperature or pressure) has the same value.

Basing on these results we conclude that in the region of the phase transition the temperature, the hydrostatic pressure or both the temperature and the hydrostatic pressure may be treated as an equivalent thermodynamic parameter.

SPONTANEOUS POLARIZATION

From the minimum condition of the Gibbs function with respect to polarization P at E = 0 we get the temperature and pressure dependence of the spontaneous polarization

$$P_s^2 = \left[\frac{\alpha}{\beta}(T_c + \Omega \cdot p - T)\right], \qquad (7)$$

i.e. the spontaneous polarization square at constant pressure (temperature) is a linear function of temperature (pressure).

Differentiating Eq.(7) with respect to pressure p we get PEC η, i.e. the coefficient linking the spontaneous polarization changes with pressure

$$\eta = \frac{\alpha\,\Omega}{\beta}\left[\frac{\alpha}{\beta}(T_c - \Omega \cdot p - T)\right]^{-1/2} \qquad (8)$$

From Eq. 8 it is clearly seen that the pressureelectric effect can be observed in a ferroelectric (polar) phase, only. Pressure dependence of coefficient η for MAPBB crystals calculated from Eq. 8 for different temperatures T (the used value of the coefficients $\alpha = 5.6 \cdot 10^7\ Vm/CK$, $\beta = 1.6 \cdot 10^{12}\ Vm^5C^{-3}$ and $\Omega = 58K/GPa$) is presented in the Fig.5. This dependence is similar to the temperature dependence of the pyroelectric coefficient.

In the region of the phase transition, coefficient η for **MAPBB crystals is a few orders higher (usually 3–4 orders) than that observed in a linear pyroelectrics.** From this reason pressureelectric phenomenon of ferroelectric crystals may be useful for conversion from elastic to the the electric energy and detection of pressure changes.

PRESSUREELECTRIC DETECTOR (CONVERTER) OF HYDROSTATIC CHANGES

The changes of gas or liquid pressure dp surrounding a plate cut from polar (ferroelectric) crystal caused its polarization change

$$dP_s = \eta\, dp. \qquad (9)$$

The electric current intensity in the load resistance R_o (cf. Fig.6)

$$I = S\,\eta\,\frac{dp}{dt} \qquad (10)$$

is proportional to the velocity of the pressure changes dp/dt. These detectors may be used to measurements for pressure changes in an engine cylinder or in the elastic medium in

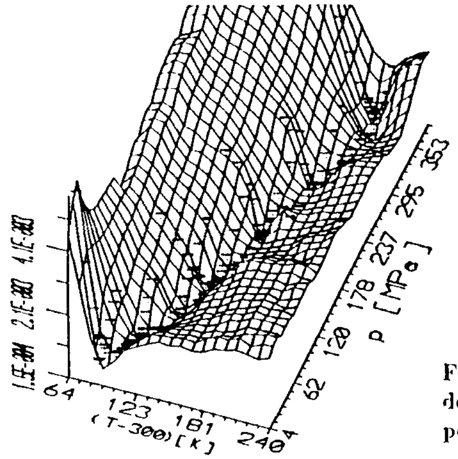

Fig.1. Pressure and temperature dependence of reverse dielectric permittivity of MAPCB crystals.

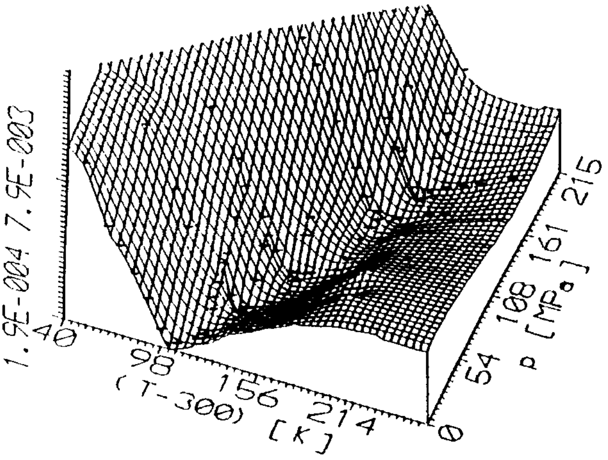

Fig.2. Pressure and temperature dependence of reverse dielectric permittivity of MAPBB crystals.

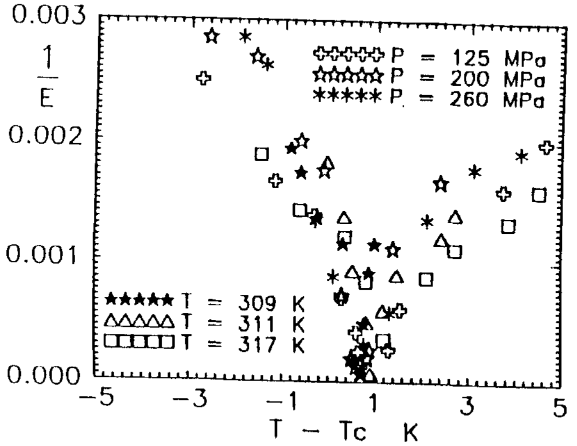

Fig.3. Reverse dielectric permittivity of MAPCB crystals as a function of $\Delta T = T - T_c(p)$, the results obtained form isobars and isoterms.

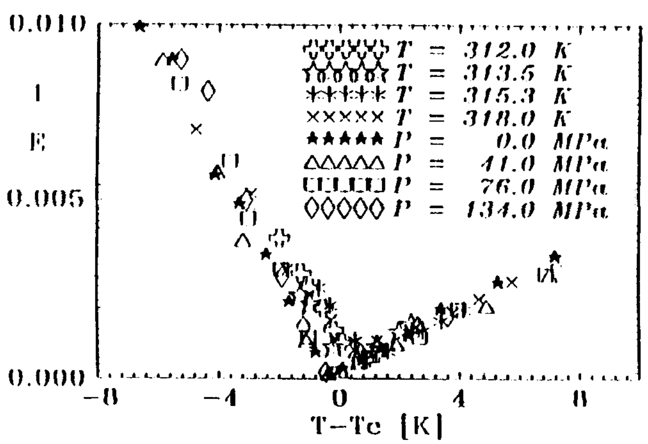

Fig.4. Reverse dielectric permittivity of MAPBB crystals as a function of $\Delta T = T - T_c(p)$, the results obtained form isobars and isotherms.

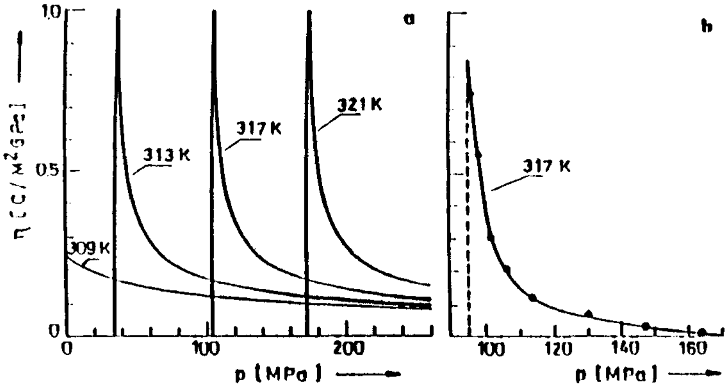

Fig.5. Pressure dependence of PEC of MAPBB crystals for different temperatures calculated from Eq. 8 - (a) and its comparision with experimental results - (b).

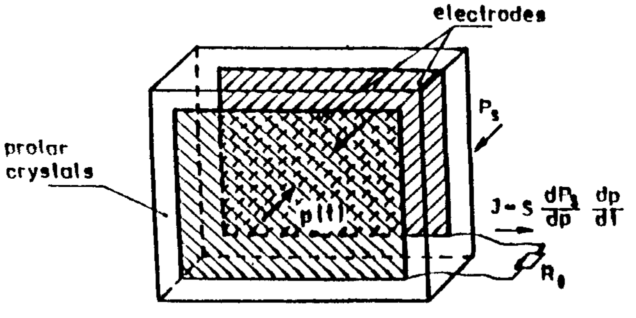

Fig. 6. Schematic view of the pressureelectric sensor of hydrostatic pressure changes.

which the explosion waves are propagated. Its sensitivity depends on the area of electrodes S and the coefficient η. The response time is determined by the sound velocity in the sensor and electric time constant of the circuit, only.

In order to detect the absolute value of the pressure p we must measure electric charge Q flowing through the external circuit

$$Q = S\eta \int_{p_1}^{p_2} dp \tag{11}$$

This detector may be treated as an electric current source of the intensity given by Eg. (10). For sufficiently large pressure changes velocity and large electrodes area S the electric energy generated by the device can takes a level interesting for applications.

The pressure dependence of pressureelectric coefficient η (Fig 5) may be applied to detect a certain hydrostatic pressure limit excess. It is worth noticing that pressure threshold may be continuously adjusted by the sensor temperature.

REFERENCES

1. R. Jakubas, *Solid State Commun.*, 69, 267 (1989).
2. R. Jakubas, L. Sobczyk, J. Lefebvre, *Ferroelectrics*, 100, 143 (1989).
3. J. Matuszewski, R. Jakubas, L. Sobczyk, T. Glowiak, *Acta Cryst.*, C46, 1385 (1990).
4. A. Miniewicz, R. Jakubas, C. Ecolivet, A. Girard, *J.Raman Spectr.*,20, 381 (1989).
5. G.A. Samara, *J. Phys. Soc. Jpn. (suplement)*, 28, 393 (1970).
6. J. Mroz, R. Poprawski, A. Kolarz, R. Jakubas, *Solid State Commun.*, 76, 821 (1990).
7. J. Mroz, R. Poprawski, R. Jakubas., *Polish J. of Chemistry* (1992) (in press).
8. F. Jona, G. Schirane,*Phys. Rev.*, 117, 139 (1960).
9. G.G. Leonidova, N.P.Nietiesova, T.R. Volk, *Fiz. Tverd. Tela*, 9, 593 (1967).
10. R. Cach, R. Jakubas, *Ferroelectrics*,108, 121 (1990).
11. R. Poprawski, *Ferroelectrics*, (in press).