FLUCTUATIONS OF COMPOSITION AND PHASE TRANSITION IN FERROELECTRIC Sb $Se_{0.40}S_{0.60}I$ (*)

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ABSTRACT — Pyroelectric coefficient (λ) was investigated in crystals of Sb $Se_xS_{1-x}I$ and a notorious broadening of the transition when x increases is verified. Spontaneous polarization (P_s) for Sb $Se_{0.40}S_{0.60}I$ is deduced from λ and the broadening of the transition is analised by assuming a non-homogeneous distribution of Se atoms through the sample.

1 — INTRODUCTION

SbSI exhibits a very sharp ferro-paraelectric phase transition of displacive type around 293 K under atmospheric pressure [1]-[4]. On substituting sulfur atoms by selenium, the order of the transition changes from first to second order for a selenium concentration larger than 0.33 ± 0.03, and the Curie temperature decreases almost linearly with Se concentration, with a large slope, $dT_C/dx \simeq -330$ K [5], [6]. It will then be expected that even small variations of x around a mean value will have a strong effect on the broadening of the phase transition on mixed compounds Sb $Se_xS_{1-x}I$.

2 — EXPERIMENTAL RESULTS

We studied the pyroelectric effect on vapour grown samples of Sb $Se_xS_{1-x}I$ by measuring the potential difference originated

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across a known short-circuiting resistance as the samples were heated at constant rates (dT/dt) from about 40 K below the respective Curie temperatures (T_C) up to some degrees above it. The samples were previously polarized along the c-axis while being cooled down and the electric field was removed when actually measuring the pyroelectric effect. The short-circuiting resistance was kept at a constant temperature thus allowing the determination of the discharging current (I) arising from the changes in the spontaneous polarization (P_s) of the samples on heating. An increase in the temperature of a ferroelectric crystal of cross section S will cause a diminution of P_s related to the current flowing in the external circuit by

$$I = S \left| \frac{dP_s}{dT} \right| \cdot \frac{dT}{dt}$$

The pyroelectric coefficient $\lambda = | dP_s/dT |$ may be evaluated from this relation. The results for various samples of $Sb\ Se_xS_{1-x}I$ are displayed in Fig. 1,and show that, as *x* increases, there is a remarkable broadening of the transition. This behaviour has been often associated with a diffuse phase transition and may be due to

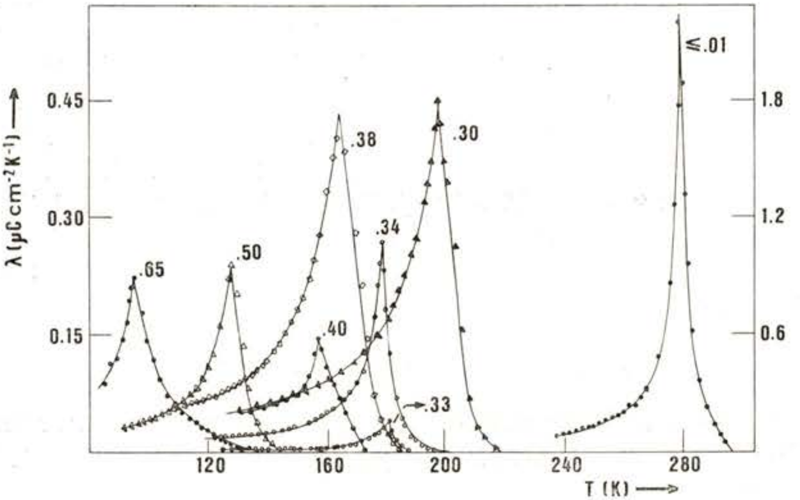

Fig. 1 — Temperature dependence of pyroelectric coefficient $\lambda = | dP_s/dT |$ for $Sb\,Se_xS_{1-x}I$ ($x \leqslant 0.01$, $x = 0.30$, $x = 0.33$, $x = 0.34$, $x = 0.38$, $x = 0.40$, $x = 0.50$, $x = 0.65$) . The right hand side scale applies to the $x \leqslant 0.01$ curve.

structural disorder, internal stresses, thermal and composition fluctuations. By means of a simple model we have tried to study the effect of composition fluctuations on the broadening of the transition and we applied these results to $Sb\,Se_{0.40}S_{0.60}I$.

Spontaneous polarization may be deduced from the pyroelectric coefficient by

$$P_s(T) = \int_{\tau}^{T} \lambda(T)\, dT$$

where $\lambda(\tau) = 0$. The resulting temperature dependence of spontaneous polarization of $Sb\,Se_{0.40}S_{0.60}I$ can be seen in Fig. 2.

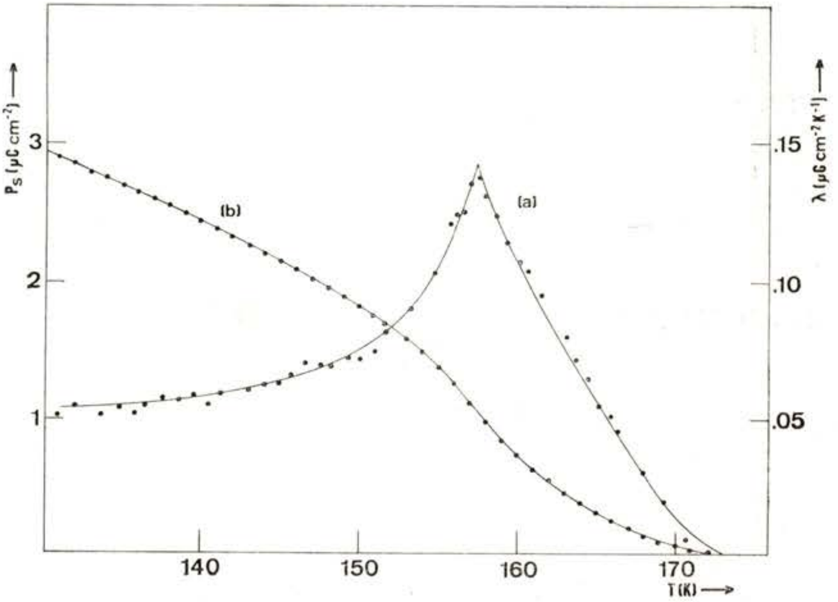

Fig. 2 — (a) Temperature dependence of pyroelectric coefficient $\lambda = |dP_s/dT|$ for $Sb\,Se_{0.40}S_{0.60}I$; (b) Temperature dependence of spontaneous polarization $P_s(T)$ for $Sb\,Se_{0.40}S_{0.60}I$.

According to Landau's theory, for a second order transition, occuring at T_0, the squared spontaneous polarization, $P_s^2(T)$, may be approximately represented by [7]

$$P_s^2(T) = A\,(T_0 - T) \qquad \text{for } T \leqslant T_0$$
$$P_s^2(T) = 0 \qquad \text{for } T > T_0$$

A plot of $P_s^2(T)$ versus T may be seen in Fig. 3 and shows that this representation is fairly good up to a few degrees below T_0.

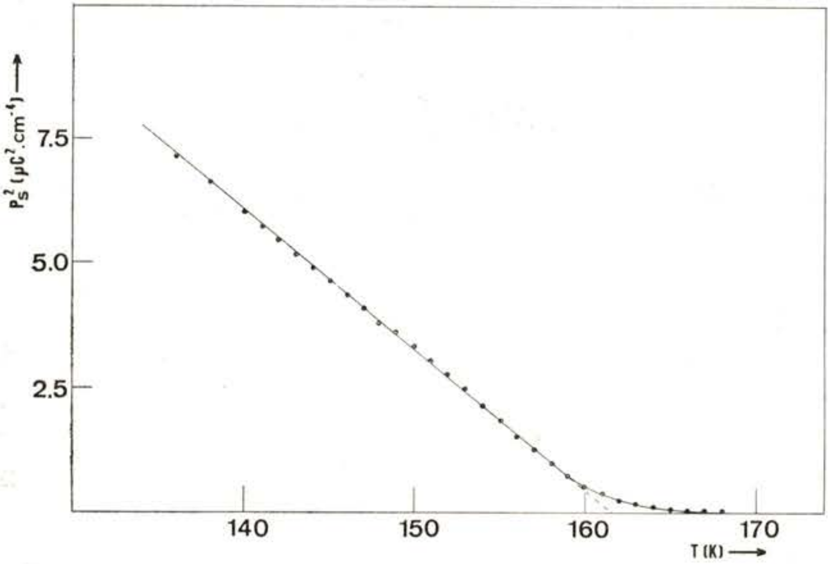

Fig. 3 — Temperature dependence of squared $P_s(T)$ for Sb $Se_{0.40}S_{0.60}I$.

3 — THEORETICAL MODEL

In the following we analyse the experimental data concerning Sb $Se_{0.40}S_{0.60}I$ using a model in which we consider the crystal formed by non-interacting regions, each with a transition temperature T_0. This is, of course, a simplifying hypothesis since the real situation is certainly more complicated and these individual regions will not be, in practice, as independent as we are assuming but will interact with each other via depolarising fields, elastic strains or thermal fluctuations.

The usual procedure [8], [9] has been to define a density of probability, which we will call $g(T_0)$, and to consider the measured values of macroscopic properties of the crystal as some kind of average over the different regions of the crystal. A thermodynamical approach of the free energy with an apparent local field in the polarization direction has already been tried to fit experimental data in Co-doped barium titanate, but without much success [9]. The fitting was better when using a truncated gaussian distribution of the Co-concentration. Taking these results into account we did not try the free energy approach.

Let T_m and T_M be the limiting transition temperatures; the probability density for finding a region of transition temperature in the vicinity of T_0 will be defined to satisfy the conditions

$$g(T_0) \neq 0 \text{ only for } T_M > T_0 > T_m$$

and, of course,

$$\int_{T_m}^{T_M} g(T_0)\, dT_0 = 1 .$$

If $P_s(T)$ represents the spontaneous polarization, at temperature T, of the region of the crystal whose transition temperature is T_0, the experimental value, measured over the whole crystal, will be an average value of $P_s(T)$, evaluated over the regions of the crystal still polarized at that temperature.

We have used two different approaches. In one of them we evaluated the average value of the square of the polarization (*a*) and in the other the average of the polarization itself (*b*).

a) Evaluation of $< P_s^2(T) >$

According to the way we defined $g(T_0)$, T_m and T_M the evaluation of $< P_s^2(T) >$ will give

$$< P_s^2(T) > = A \int_{T_m}^{T_M} (T_0 - T)\, g(T_0)\, dT_0 \quad \text{for } T < T_m$$

$$< P_s^2(T) > = A \int_{T}^{T_M} (T_0 - T)\, g(T_0)\, dT_0 \quad \text{for } T_m < T < T_M$$

$$< P_s^2(T) > = 0 \qquad \text{for } T > T_M$$

If we choose for $g(T_0)$ any function symmetric around T_C and duely normalized we will have, for $T < T_m$

$$\begin{aligned} < P_s^2(T) > &= A \int_{T_m}^{T_M} T_0\, g(T_0)\, dT_0 - A\,T \int_{T_m}^{T_M} g(T_0)\, dT_0 \\ &= A < T_0 > - A\,T = A\,(T_C - T) \end{aligned}$$

For simplicity we have chosen $g(T_0)$ as a parabolic function, symmetric around T_C, defined between $T_m = T_C - \Theta$ and $T_M = T_C + \Theta$ by

$$g(T_0) = -\frac{3}{4\,\Theta^3}\,[(T_0 - T_C)^2 - \Theta^2]$$

We obtain

$$< P_s^2(T) > = A\,(T_C - T) \qquad T < T_m$$

$$< P_s^2(T) > = \frac{A}{16\,\Theta^3}\,[(T_C + \Theta) - T]^3\,[T - (T_C - 3\,\Theta)]$$

$$< P_s^2(T) > = 0 \qquad T > T_M$$

The pyroelectric coefficient (λ), here taken as

$$\lambda = \frac{d}{dT}\,[< P_s^2(T) >]^{1/2}$$

has a maximum at a temperature

$$T_{max} = T_C - (2 - \sqrt{3})\,\Theta$$

To apply this model to our experimental results we assumed that $< P_s^2(T) > \simeq < P_s(T) >^2 \simeq P^2_{exp}(T)$. From the plot of P^2_{exp} versus T (Fig. 3) we deduced the values $A = 0.287\ \mu C^2\,cm^{-4}\,K^{-1}$, $T_C = 161.4$ K and $\Theta = 7.9$ K. The fit may be seen in Fig. 4, curve (a): it shows a good agreement from 130 K up to 145 K. It also seems to indicate that a larger value of Θ should be used, as does the difference we find between the experimental value $T_{max} = 157.5$ K and the predicted value $T_C - (2 - \sqrt{3})\,\Theta = 159.3$ K. However, a theoretical curve using a larger value of Θ may also be seen in the same figure, curve (b), and it does not show a better agreement. This may be due either to the simplicity of the function we assumed for $g(T_0)$ or to the use of $< P_s^2(T) >$ instead of $< P_s(T) >^2$. In Fig. 5 we can see a

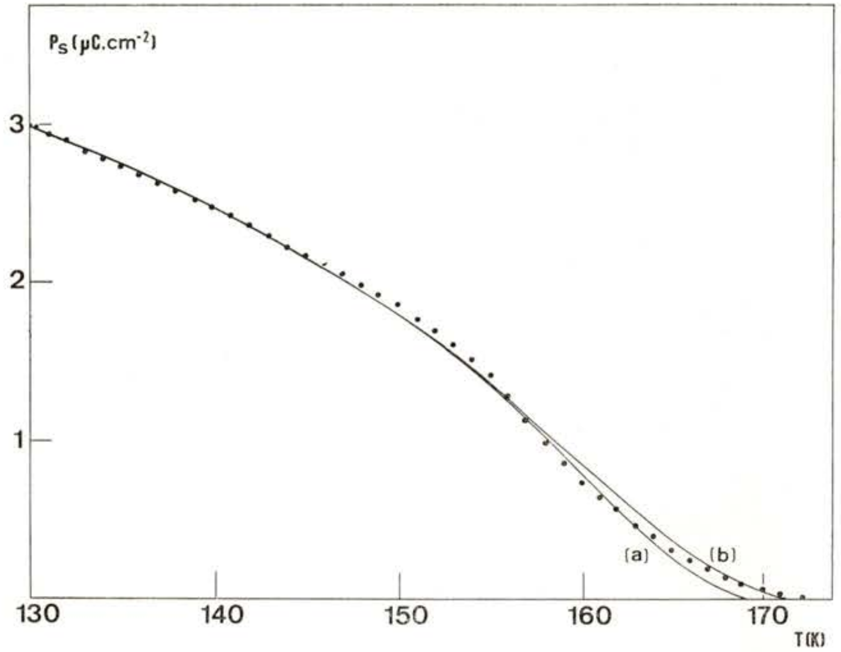

Fig. 4 — Temperature dependence of $P_s(T)$: Full circles, experimental results for Sb $Se_{0.40}S_{0.60}I$; Full lines, calculated values of $[<P_s^2(T)>]^{1/2}$ by taking a parabolic function as a density of probability.

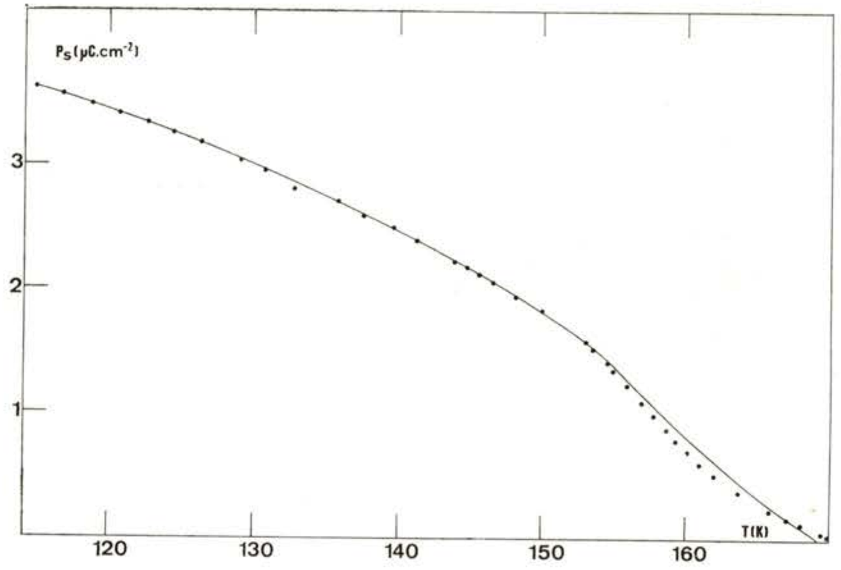

Fig. 5 — Temperature dependence of $P_s(T)$: Full circles, experimental results for Sb $Se_{0.40}S_{0.60}I$; Full line, calculated values of $[<P_s^2(T)>]^{1/2}$ by taking a truncated gaussian function as a density of probability.

another theoretical fit by taking a truncated gaussian function as a density of probability. As the situation has not improved significantly we tried another approach.

b) Evaluation of $< P_s(T) >$

$P_s(T)$ may be written

$$P_s(T) = A^{1/2}\sqrt{T_0 - T} \qquad \text{for } T < T_0$$

$$P_s(T) = 0 \qquad \text{for } T > T_0$$

We will now define $g(T_0)$ by

$$g(T_0) = \frac{1}{\Phi_0}\exp\left[-\frac{(T_0 - T_C)^2}{\Theta^2}\right] \qquad T_m < T < T_M$$

$$g(T_0) = 0 \qquad \text{elsewhere}$$

where

$$\Phi_0 = \int_{T_m}^{T_M} \exp\left[-\frac{(T_0 - T_C)^2}{\Theta^2}\right] dT_0 .$$

The average value of P_s will then be

$$< P_s(T) > = \frac{A^{1/2}}{\Phi_0}\int_{\zeta}^{T_M} \sqrt{T_0 - T}\,\exp\left[-\frac{(T_0 - T_C)^2}{\Theta^2}\right] dT_0 ,$$

where $\zeta = T_m$ for $T < T_m$ and $\zeta = T$ for $T_m < T < T_M$; and

$< P_s(T) > = 0$ for $T > T_M$.

All integrals shown were evaluated numerically. The fit to experimental results was done by trial and error: the best fit was found for $T_C = 163.0$ K and $\Theta = 8.5$ K and may be seen in Fig. 6 (b). Although some discrepancies persist the agreement has improved significantly. In Fig. 7 we can see a plot of $< P_s(T) >^2$ versus T calculated from the expression just given

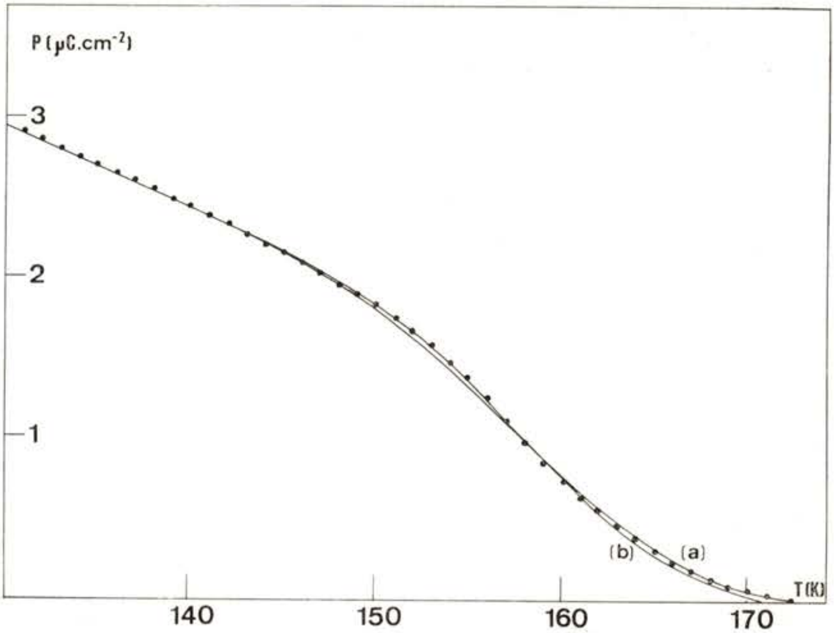

Fig. 6 — Temperature dependence of $P_s(T)$: Full circles, experimental points for $Sb\,Se_{0.40}S_{0.60}I$; Full lines, theoretical fit obtained by using a truncated gaussian function as a density of probability, (a) $\Theta = 10$ K; (b) $\Theta = 8.5$ K.

with an arbitrarily fixed value for A and for different values of Θ. As we can see, not too near the transition temperature $< P_s(T) >^2$ is still fairly well represented by a straight line, $< P\ (T) >^2 = \text{const.}\ (T_0 - T)$, which intercepts the T-axis the farther from T_C, the larger the value of Θ.

4 — CONCLUSIONS

In a diffuse phase transition the spreading of the transition temperature in a finite range of temperature has been ascribed to thermal and composition fluctuations, internal stresses, dispersion of the c-axis orientation and so on. As we observe a broadening of the transition in mixed compounds $SbSe_xS_{1-x}I$

increasing with x we think that fluctuations of Se composition may be an important reason for the diffuse character of the transition in those compounds. The model used explains two features of the diffuse phase transition, namely that the pyroelectric effect does not go to zero just at T_0 but some degrees above it, and that far from the transition the averaged spontaneous polarization of the crystal will still behave approximately as if the transition temperature was unique.

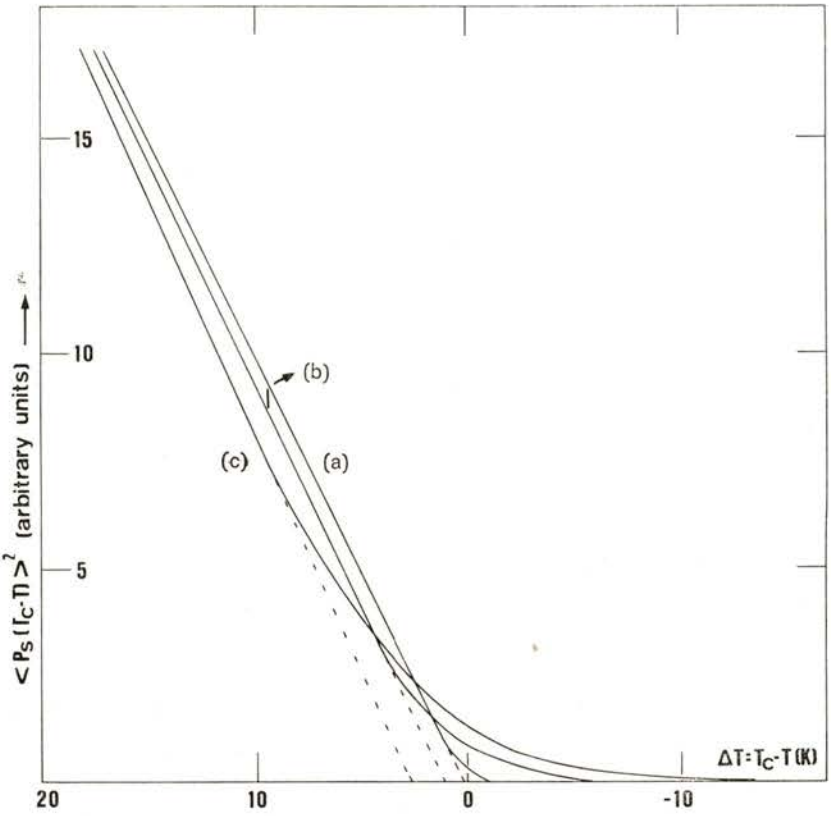

Fig. 7 — Temperature dependence of $< P_s(T_C - T) >^2$ obtained by using a truncated gaussian function as a density of probability, $A = 10$ (arbitrary units), (a) $\Theta = 1$ K; (b) $\Theta = 10$ K; (c) $\Theta = 15$ K.

The value of 8.5 K found for Θ, corresponds to a fluctuation of Se concentration of some 2.5 % around a mean value $\bar{x} \simeq 0.40$. This seems a reasonable value for composition fluctuations since, as we have already pointed out, the variation of the transition temperature T_C with the concentration x of Se is quite high (33 K for $\Delta x = 0.1$), so we expect that even small fluctuations of x will produce noticeable effects on the polarization of the crystal. Work is in progress to obtain a better fit to experimental data using other trial functions.

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REFERENCES

[1] KIKUCHI, A, OKA, Y. and SAWAGUCHI, E., *J. Phys. Soc. Japan* **23**, 337 (1967) and references therein.

[2] FURMAN, E., BRAFMAN, O., and MAKOVSKY, J., *Phys. Rev.* **B8**, 2341 (1973).

[3] TENG, M. K., BALKANSKI, M., MASSOT, M. and ZIOLKIEWICZ, M. K., *Phys. Status Solidi* (b) **62**, 173 (1974).

[4] CHAVES, R., AMARAL, H. and ZIOLKIEWICZ, S., *J. Physique,* **41**, 259 (1980).

[5] NITSCHE, R., ROETSCHI H., WILD, P., *Appl. Physics Letters* **4**, 2101 (1964).

[6] CHAVES, M. R., AMARAL, M. H., (to be published).

[7] LINES, M. E., GLASS, A. M., *Principles and Applications of Ferroelectrics and Related Materials,* Clarendon Press, Oxford 1977.

[8] YURKEVICH, V. E., ROLOV, B. N., *Czech J. Phys.* **B25**, 701 (1975).

[9] GODEFROY, G., CHATRY, P., BENGUIGUI, L., *Ferroelectrics* **34**, 169 (1981).