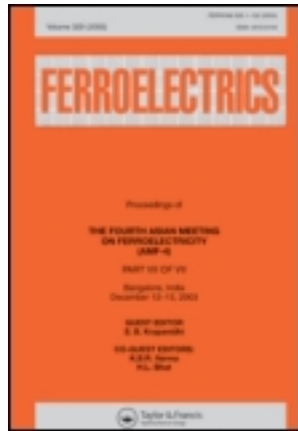


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IMPROPER FERROELECTRICS FOR PYROELECTRIC DETECTION OF INFRARED RADIATION

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The absence of dielectric divergence in improper ferroelectrics makes it possible to obtain a high pyroelectric figure of merit near their transition temperature. Results of measurements carried out as a function of temperature on representatives of three classes of improper ferroelectrics: rare-earth molybdates, propionates, and boracites, show that in each of these the figure of merit rises to a peak value which is superior to that of triglycine sulfate. Analysis of the experimental results using a Landau type free-energy model yields an estimate of the optimum figure of merit obtainable.

INTRODUCTION

In the characterization of the performance of pyroelectric materials as infrared detectors, the ratio, $p/\epsilon c$, of the pyroelectric coefficient, p , to the product of the permittivity, ϵ , and the volume specific heat, c , is of primary importance. This ratio determines the maximum responsivity bandwidth product obtainable for a small-area (point) detector¹, and also the signal-to-noise ratio obtainable in the pyroelectric vidicon designs currently in use.^{2,3} During the last decade many pyroelectrics have been investigated in search of improved materials for use in point detectors and vidicons.^{3,4} Efforts were concentrated on proper ferroelectrics of the TGS-TGFB family. In these materials, the increase in the pyroelectric coefficient obtained by approaching the ferroelectric-paraelectric transition temperature is accompanied by an even faster increase in the dielectric constant so that the material's figure of merit, $M=p/\epsilon c$, decreases as the transition point is approached.⁵ The thermodynamic model of Devonshire predicts the relationship⁶

$$p/(\epsilon-1) = P_s/C, \quad (1)$$

where P_s is the spontaneous polarization and C the Curie constant. Since, in general, ϵ is much greater than 1, this model predicts that M decreases with temperature at least as fast as P_s .

The use of improper ferroelectrics in pyroelectric detectors offers the possibility of overcoming this limitation. The relatively low permittivity and the absence of dielectric divergence in these materials makes it possible to obtain a high figure of merit near their transition temperature.

During a broad study of improper ferroelectrics, we have investigated pyroelectric detection properties of three different classes of crystals: rare-earth molybdates, propionates and boracites. In this paper we present experimental

results obtained in terbium-molybdate, $Tb_2(MoO_4)_3$ (TMO), dicalcium-lead-propionate, $Ca_2Pb(CH_3CH_2COO)_6$ (DLP), and iron-iodine-boracite, $Fe_3B_7O_{13}I$ (FIB). In each of these materials the figure of merit was determined by separate measurements of p , ϵ , and c , and by a direct measurement of the ratio $p/\epsilon c$. The pyroelectric coefficient was measured using the dc technique of Byer and Roundy and the ac technique of Chynoweth. The dielectric constant was measured at 8 kHz in a field of ~ 10 V/cm. A direct measurement of $p/\epsilon c$ was accomplished by a modification of the dynamic technique of Chynoweth.

EXPERIMENTAL RESULTS

Figure 1 shows the temperature dependence of p in TMO, FIB, and unannealed DLP. The three materials exhibit a similar pyroelectric behavior: p rises as the transition point, T_c , is approached; T_c for TMO, FIB, and DLP is $161^\circ C$, $72.4^\circ C$, and $54^\circ C$, respectively. Due to the high internal biasing field in unannealed samples of DLP, the pyroelectric coefficient of this material does not vanish above the transition point. Unlike the pyroelectric behavior, the temperature dependence of the dielectric constant of these materials is qualitatively different (Figure 2). The dielectric behavior of DLP is similar to that of a biased TGS. At the transition point the dielectric constant of TMO shows a discontinuous jump downward. This is quite opposite of FIB whose dielectric constant exhibits a discontinuous jump upward at T_c . Common to these three materials is the low value of ϵ and the small dielectric anomaly in the transition region.

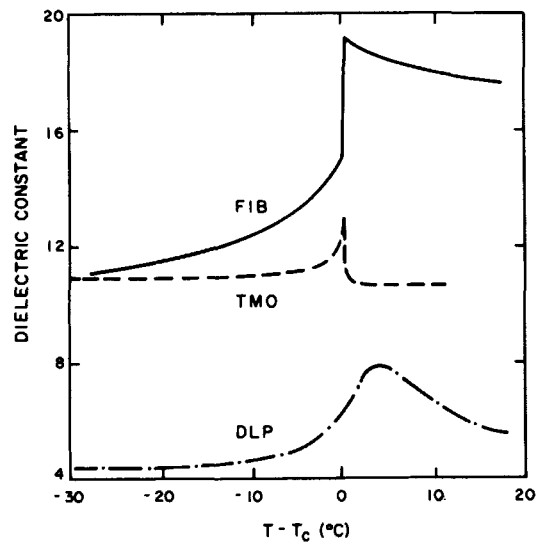
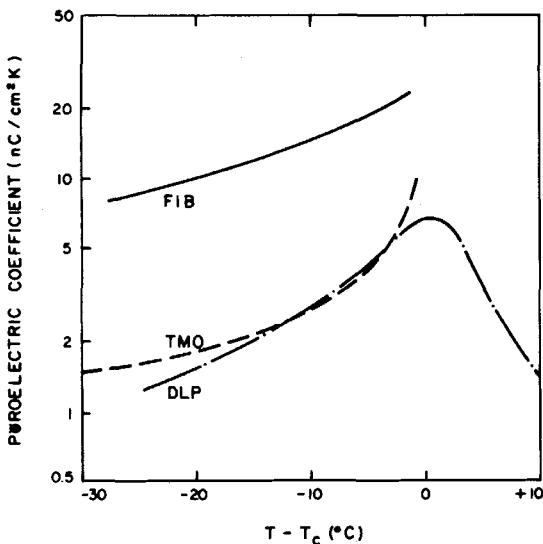


FIGURE 1. Temperature dependence of the pyroelectric coefficient in terbium molybdate, iron-iodine boracite, and unannealed dicalcium lead propionate.

FIGURE 2. Dielectric constant vs. temperature for terbium molybdate, iron-iodine boracite and unannealed dicalcium lead propionate.

Figure 3 shows the temperature dependence of $p/\epsilon c$ in TMO, DLP, and FIB as measured by the dynamic method. In sharp contrast to the behavior exhibited by proper ferroelectrics such as TGS, in these materials $p/\epsilon c$ increases in the same manner as p as the transition point is approached. This result is expected on the basis of the small increase in dielectric constant near the transition. In each of these materials M rises to a value which is distinctly higher than that of TGS. In both TMO and FIB the maximum value of M is obtained at T_c ; however, the FIB maximum is both higher and broader. In unannealed DLP the transition is blurred due to the intrinsic biasing field, and the maximum value of M changes only slightly in a temperature interval of several degrees around the maximum.

ANALYSIS AND DISCUSSION

Following the theoretical works of Levanyuk and Sannikov⁹, Dvorak¹⁰, Aizu¹¹, Gufan and Sakhnenko¹², and Kobayashi¹³, we analyzed our experimental data on the basis of a Landau type free-energy model. Our analysis was based on a simplified free energy

$$F(\eta, P, T) = F_o(T) + \beta(T - T_\eta)\eta^2/2 + \gamma\eta^4/4 + \delta\eta^6/6 + F_c(\eta, P) + \chi_o^{-1}P^2/2 - EP \tag{2}$$

where η is the order parameter, T , P , and E are the temperature, polarization, and electric field, respectively, $F_c(\eta, P)$ represents a coupling of η and P . For TMO, DLP, and FIB we assumed coupling terms $f\eta P$, $f\eta P$, and $(f_1\eta^2 P + f_2\eta^2 P^2)$ respectively.

With the coupling term $f\eta^2 P$ the free energy given in Eq. (2) yields the following expressions for p , ϵ , and c at zero field:

$$p = \frac{1}{2}K (T_1 - T)^{-1/2}, \tag{3}$$

$$\epsilon = \epsilon_p + K_1 (T_1 - T)^{-1/2}, \tag{4}$$

$$c = c_o + (K^2/4K_1)T (T_1 - T)^{-1/2}, \tag{5}$$

where $K = -f\chi_o(\beta/\delta)^{1/2}$, $K_1 = (f\chi_o)^2/(\beta\delta)^{1/2}$, $T_1 = T_c + (\gamma - 2f^2\chi_o)^2/4\beta\delta > T_c$, $\epsilon_p = 1 + \chi_o$, and $c_o = -T(\partial^2 F/\partial T^2)$. The predictions of Eqs. (3) - (5) have been verified in detail for TMO.¹⁴ Analysis of the temperature dependence of $M = p/\epsilon c$ shows that M attains a maximum at T_c unless unrealistically small values of ϵ_p and c_o are assumed. Optimizing M at T_c with respect to $(T_1 - T_c)$ and the ratio K/K_1 , yields an optimum figure of merit $M_{opt} = (16\epsilon_p c_o T_c)^{-1/2}$. Using the typical values $\epsilon_p = 10$ and $c_o = 2J/cm^3 K$ we obtain prediction for M_{opt} of 1.1×10^4 cm²/C for $T_c = 40^\circ C$. This value is about 2.5 times the value of M_{opt} in TGS at room temperature.

The free energy appropriate to DLP is that of a second-order pseudoproper ferroelectric (namely, the coupling term is $f\eta P$ and $\gamma > 0$ so we may take $\delta = 0$). Expressions for p , ϵ , and c similar to those for a second order proper ferroelectric are readily obtained from this free energy. These predictions are in good qualitative agreement with our measurements as well as certain published data. Analysis of the figure of merit for $E=0$ shows that M has a maximum as a function of temperature which is given by: $M_{max} = \beta/2c_o (2\epsilon_p \gamma)^{1/2}$. Note that unlike the case for the

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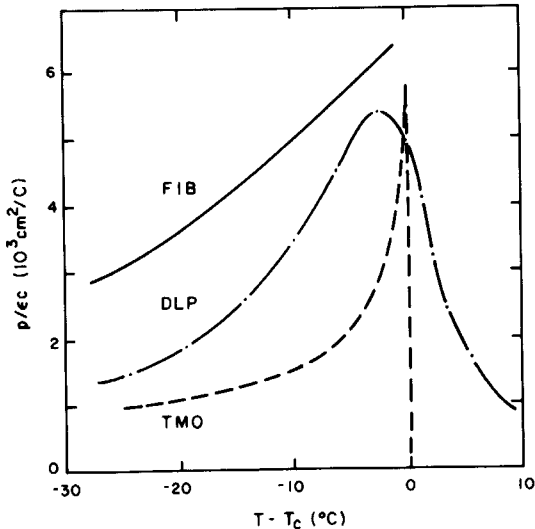


FIGURE 3. Temperature dependence of p/ϵ in terbium molybdate, iron-iodine boracite, and unannealed dicalcium lead propionate.

On the basis of the experimental data obtained in TMO, DLP, and FIB and their analysis, we conclude that improper ferroelectrics have a potential for greatly improved pyroelectric figure of merit.

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REFERENCES

1. E.H. Putley, in Semiconductors and Semimetals, edited by R.K. Willardson and A.C. Beer (Academic, New York, 1970), Vol. 5, P 259.
2. R.G.F. Taylor and H.A.A. Boot, Contemp. Phys. **14**, 55 (1973); B. Singer, Adv. Image Pickup Display **3**, 1 (1977).
3. L.E. Garn and E.J. Sharp, IEEE Trans. Parts Hybrids Packag. PHP-10, 208 (1974).
4. S.T. Liu and D. Long, Proc. IEEE **66**, 14 (1978).
5. A. Shaulov, M.I. Bell, and W.A. Smith, J. Appl. Phys. **50**(7), 4913 (1979).
6. S.T. Liu and J.D. Zook, Ferroelectrics **7**, 171 (1974).
7. F.G. Ullman, B.N. Ganguly, and J.R. Zeidler, J. Electron Mater. **1**, 425 (1972).
8. M. Takashige, H. Iwamura, S. Hirotsu, and S. Sawada, Ferroelectrics **11**, 431 (1976).

molybdates M_{\max} has no natural optimum with respect to the parameters which characterize the phase transition.

The free energy proposed^{10,12} for the boracites embodies a coupling term $f_1 \eta^2 P + f_2 \eta^2 P^2$. Comparison of our experimental results with the predictions of this free energy is in progress. Thus far, the experimental behavior of ϵ in FIB and NiBr boracite is in good agreement with the theoretical predictions of the free energy when we make a certain hypothesis on the relative magnitudes of f_1 and f_2 . Within this approximation, the pyroelectric coefficient can be related to the rate of change of ϵ with temperature:

$$p = (\Delta P / \Delta \epsilon) (d\epsilon / dT), \quad (6)$$

where ΔP and $\Delta \epsilon$ are respectively the jumps of P_s and ϵ at T_c . Due to the large ΔP (of the order of $1 \mu\text{C}/\text{cm}^2$) obtainable in boracites, a large pyroelectric coefficient can be expected on the basis of Eq. (6). A preliminary estimate of an upper bound for the figure of merit in boracites yields a value which is much higher than the optimum value predicted for the molybdates.

9. A.P. Levanyuk and D.G. Sannikov, Sov. Phys. Sol. State 12, 2418 (1971).
10. V. Dvorak, Phys. Stat. Sol. (b) 46, 763 (1971). V. Dvorak, Czech. J. Phys. B 21, 1250 (1973). V. Dvorak, Phys. Stat. Sol. B 55, K59 (1973).
11. K. Aizu, J. Phys. Soc. Japan 31, 802 (1971).
12. Yu. M. Gufan and V.P. Sakhnenko, Sov. Phys. Sol. State 14, 1660 (1973).
13. J. Kobayashi, Y. Enomoto, and Y. Sato, Phys. Stat. Sol. (b) 50, 335 (1972).
14. M.I. Bell, A. Shaulov, Y.H. Tsuo, M. Delfino, G. Loiacono, and W. Smith, Bull. Am. Phys. Soc. 23, 197 (1978); W.A. Smith, Philips Laboratories, Final Technical Report on Contract No. DAAG-53-76-C-0053, Vol. II, 1978.

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