

HIGH PHOTOVOLTAGES IN FERROELECTRIC CERAMICS

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INTRODUCTION

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Photovoltaic effects which seem specifically connected with ferroelectricity have only a brief history. Weak steady photocurrents in flux-grown single crystals were observed by Chynoweth (ref. 1) in the middle 1950s. These were seen in connection with studies of pyroelectricity and polarization of surface layers in single crystals. A similar effect, observed by Brody and Michael Vrabel in 1968 (ref. 2), originated in pyroelectric surface regions of disordered ferroelectric ceramic barium titanate. The photo-emf's were clearly related to a remanent polarization within these layers exhibiting the same temperature dependence as this polarization. The emf's were considerably less than 1V.

A high-voltage effect was observed by Brody in polarized barium titanate ceramic in 1971 (ref. 3), and soon afterward in other polarized ferroelectric ceramics (ref. 4). The high emf was proportional to the sample length. Such a phenomenon is usually called a high voltage - bulk photovoltaic effect. High-voltage effects have been previously observed in ZnS single crystals by Merz (ref. 5). A length dependent photo-emf also appears in evaporated polycrystalline films of semiconductors in which the evaporation source was at an angle to the substrate. These are fairly well known from the work of Pensak (ref. 6) and others.

The photovoltaic effect in ferroelectric ceramics is characterized by a high photo-emf parallel to remanent polarization and proportional to its magnitude. The emf is proportional to sample length in the direction of polarization, and generally to the number of grains per unit length. A rectangular slab with electrodes on opposing edges, such as that shown in figure 1, uniformly and steadily illuminated on its unobscured face, appears as a source comprised of an intensity-saturable emf in series with a photoresistance. For saturation intensities there appears a steady short-circuit current depending linearly on intensity. The current also depends strongly on the wavelength peaking sharply for light with energy in the vicinity of the band-gap energy. Typically in these materials, this is the near ultraviolet or violet. The emf is also, but less strongly, dependent on wavelength.

We have measured the short-circuit current and photo-emf for various ceramics including barium titanate, lead metaniobate, and lead titanate - lead zirconate solid solutions, these latter with niobium, strontium and lanthanum additives. Results include emf's of 1500 V/cm in centimeter-size samples of small-grain-size $\text{Pb}(\text{Zr}_{.65}\text{Ti}_{.35})\text{O}_3$ with 7 percent lead substituted for by lanthanum - a hot pressed ceramic known as PLZT 7/65/35. In the ceramic $\text{Pb}(\text{Zr}_{.53}\text{Ti}_{.47})\text{O}_3$ plus 1 wt% Nb_2O_5 the saturation photo-emf is about 500 V/cm and the short-circuit current, for the wavelength producing the peak current, is about $1 \mu\text{A}/\text{cm}/\text{W}/\text{cm}^2$. This last material is the best material that we have measured thus far in terms of energy conversion. A short-circuited sample converts 0.06 percent of incident light to electrical energy.

From the view point for energy conversion, such a number is discouraging. However, up to the present we have done no material research and have used materials that are commercially produced for their piezoelectric or electro-optical properties. There are undoubtedly ways to increase efficiency. In this light it should be remembered that the efficiency of the first photocells using cuprous oxide did not exceed 0.1 percent (ref. 7).

The experimental results will be described in greater detail, and completing this, a mechanism for the effect will be proposed.

PHENOMENA

The steady voltage produced is proportional to the length, ℓ , between the electrodes in an arrangement such as that shown in figure 1. Dividing the sample in two equal segments along a line perpendicular to the direction of remanent polarization and placing new electrodes on the cut edges results in new samples producing photo-emf's which are one-half the original photo-emf.

An arrangement such as that shown in figure 1 can be described roughly by an equivalent circuit shown in figure 2. This circuit has a saturation photo-emf in series with the photoresistance of the illuminated sample. The sample capacitance C is across the electrodes. Figure 3 is the current-voltage characteristic of a typical illuminated ferroelectric slab. It has the form expected from the equivalent circuit in figure 2, except for the slight tendency to saturation in the lower-left quadrant. The photo-emf saturates as a function of intensity at relatively low levels of illumination. The short-circuit photocurrent is, however, linear with light intensity. Typical results showing the intensity dependence are shown in figure 4. The implication of these results and of the equivalent circuit in figure 2 is that the photoresistance is inversely proportional to intensity.

Photo-emf's and short-circuit currents for a number of ferroelectric materials are shown in table 1. The photo-emf is also a function of grain size. Results showing this are given in table 2.

The wavelength dependences of the photo-emf and photocurrent for $\text{Pb}(\text{Zr}_{.53}\text{Ti}_{.47})\text{O}_3 + 1$ wt% Nb_2O_5 shown in figure 5, are typical of these materials. The current (ordinate) is that produced by illumination contained in a small band, of about ± 10 nm, about the wavelength indicated on the abscissa. A mercury source and notch-type dichroic filters were used. The total intensity within each band was only roughly constant. Therefore, the current that has been plotted has been normalized to constant intensity - assuming that the relation between current and intensity is linear.

The photo-emf is less strongly dependent on wavelength. Results for a particular material, using notch-type dichroic filters are shown also in figure 5. These values are saturation values, independent of intensity.

Similar results for the same material using dichroic, short wavelength cutoff filters are shown in figure 6. Here it is seen that high emf's continue to be produced at wavelengths shorter and also considerably longer than the 373-nm wavelength at which the short circuit current peaks.

In the arrangement shown in figure 1 the direction of polarization, and consequently the direction of the photo-emf, is perpendicular to the direction of incidence of the light, which is also the direction in which the light is strongly absorbed. The light only enters into a region near the surface of the material. The rapidity of the absorption depends strongly on the wavelength of the light, the light becoming fully absorbed in a region closer and closer to the surface as the wavelength of the light approaches the band-gap wavelength. For shorter wavelengths, the light no longer enters the material, and light-induced emf vanishes.

Polishing the surfaces of these materials increases the transparency by decreasing the amount of diffuse reflection. Then, as expected, the magnitudes of the photocurrent and the photovoltaic conversion efficiency increase.

An emf will also be produced by the arrangement shown in figure 7, in which the front surface electrode is transparent. The emf now appears across the thickness of the material in the direction of the remanent polarization. The currents, however, are limited by the high dark-resistance of the unilluminated region of the sample.

MECHANISM

We now propose that the photo-emf results from the action of internal fields within individual ceramic grains on non-equilibrium carriers generated by illumination. These carriers move to screen the internal field. This is a change in charge distribution upon illumination, which changes the voltage across a grain from an initial value of zero to the photovoltages that are observed.

The photo-emf's appear across individual ceramic grains. What is observed as a length-dependent high photovoltage is the series sum of the photo-emf's appearing across grains, each of which is characterized by a saturation remanent polarization. The situation is shown schematically in figure 8. Individual grains are small, typically of the order of 10μ in diameter. To produce a high photovoltage-per-unit-length in the ceramic, the voltage across an individual grain need not be large. For example, the results in table 2 for $\text{Pb}_{.65}\text{Zr}_{.35}\text{Ti}\text{O}_3$ (7% La) can be explained by individual grain photovoltage of only about 0.5 V per grain. The implication of the experimental results (table 2 and figure 5) is that for the range of grain sizes investigated, the photo-emf across a grain is more or less independent of the size of the grain.

ORIGIN OF INTERNAL FIELDS

Ferroelectric ceramics are characterized by a large remanent polarization that would be expected to produce a large emf even in the dark. Such an emf is not observed even across highly insulating materials. This absence of an emf must be the result of space charge within the volume or on the surface of the individual ceramic grains. The space charge produces a potential across a grain cancelling the potential produced by the net polarization. It seems obvious that as long as there are, within a grain, charges that are free to move, any potential produced by an internal polarization will eventually vanish.

In our argument this dark zero-potential state produced by the presence of space charge is assumed to be the initial state of a ceramic grain. The absence of a net potential in the dark does not however necessarily mean the absence of internal fields. Internal fields can be expected to exist as a consequence of an extended but not uniform spatial distribution of the charges which bring the net potentials across grains to zero. These spatial distributions cannot be arbitrarily assigned but are subjected to constraints of a basic physical nature.

Were there no space charge producing a field negating the bound polarization charge, there would be a potential across a grain. The electric field within this grain would, however, be well above the dielectric breakdown strength of a real dielectric. For example, in a single-domain ferroelectric crystal of barium titanate, the spontaneous polarization is $P_s = 26 \times 10^{-2} \text{C/m}$, and the relative dielectric constant ϵ_r in the direction of polarization is 137. The maximum field in the materials would not exist for long but be reduced to some value below the dielectric strength of the material. The strong field would break down the material and a charge flow would produce a space charge distribution, resulting in a new lower value for the internal fields within the bulk of such a crystal. The fields within the space charge layers themselves do not produce an additional breakdown within the layers. The mean free path of the charges involved have now become larger than the layer thickness itself, resulting in the elimination of the breakdown phenomena, an avalanche process.

We assume that such a space-charge distribution exists within each grain. The space charge serves to reduce the potential across each grain to zero. Such charges are assumed to have limited mobility and the materials behave as insulators for ordinary-strength applied fields.

The space charge must occupy a finite volume. If these charges are localized near the surface of the crystal, then an internal field E_b exists within the bulk of the material, and additional fields E_s exist in the space charge regions near the surface.

Reasons for hypothesizing that these space-charge regions are near the surface of real crystals with the charge distributed within a surface layer of small thickness ℓ are the following. (First, the surface regions ferroelectric crystals are characterized by regions whose dielectric, ferroelectric, and thermodynamic properties differ markedly from that of the bulk and these differences are best explained by the existence of strong fields in this region that would be produced by the space charge. There is a considerable body of information in the literature supporting the existence and delineating the properties of these layers (see, for example, ref. 8). Second, the interplay of space charge and the very nonlinear dielectric constant of ferroelectrics would be expected to localize space charge in a low dielectric-constant layer near the surface. In ferroelectrics unusually high, low-field relative dielectric constants (of the order of 1000) can be expected to be reduced in value with increasing field strength. Thus, charge in a region reduces the region's dielectric constant of *that region*, and increasing its field strength. This feedback mechanism can be shown to localize charge within a layer (ref. 9).

A schematic description of a hypothetical grain, with space charge regions of thickness s , and a bulk region of thickness ℓ , is shown in figure 9. The grain has within the bulk region a dielectric constant ϵ_b and uniform remanent polarization P_0 . Within the surface layers the dielectric constant, ϵ_s , is considerably less than that of the bulk. There are also remanent polarizations in the surface regions $P_s(x)$. These will generally be parallel to the bulk polarization at one end and anti-parallel at the other end. It is the space charge that produces the high fields which reduce the highly nonlinear

dielectric constant of the bulk to the lesser value ϵ_s in the surface layers, and also produce a remanent polarization by ordering domains within the surface. The fields within the grain can be easily calculated using the two-dimensional model shown in figure 10.

The remanent polarizations within the various regions are assumed to be uniform within these regions. This is done to simplify the calculations. Again, only for simplicity, the polarizations in the surface layers and the bulk are assumed equal in magnitude (that is, $P_s(x) = P_o$). The space-charge densities $\pm n_o e$ are also assumed uniform and equal in magnitude. The polarizations are equivalent to four bound-surface charge densities,

$$\sigma_1 = P_o, \quad \sigma_2 = -2 P_o, \quad \sigma_3 = 0, \quad \sigma_4 = P_o$$

From Gauss's law, the electric fields are

$$E_1 = \frac{1}{\epsilon_s} (P_o + n_o e x), \quad (1)$$

$$E_2 = \frac{1}{\epsilon_b} (-P_o + n_o e s), \quad (2)$$

$$E_3 = \frac{1}{\epsilon_s} [-P_o + n_o e (L-x)] \quad (3)$$

We have assumed that the voltage across the crystal vanishes

$$\int_0^{l+2s} E(\alpha) d\alpha = 0 \quad (4)$$

The variables n_o and s , from this and the three preceding equations, must be related by the expression

$$n_o e s = \frac{P_o}{1 + \frac{\epsilon_b}{\epsilon_s} \frac{s}{l}} \quad (5)$$

and the bulk field must be

$$E_2 = -\frac{P_o}{\epsilon_b} \left(\frac{\frac{s}{l} \frac{\epsilon_b}{\epsilon_s}}{1 + \frac{s}{l} \frac{\epsilon_b}{\epsilon_s}} \right) \quad (6)$$

ORIGIN OF THE PHOTO-EMF

To obtain a photo-emf of the correct sign it is now assumed that illumination has the effect of producing charges that screen only the internal field, E_2 , causing it to vanish. The negative voltage vanishes and a positive potential appears across the sample. The light makes the sample look more positive. This is exactly what happens using the conventions of figure 10, as the result of a thermally produced decrease in polarization of the bulk. The pyroelectric voltage is in the same direction as the photovoltage. This is what is actually observed.

Thus, light-generated free electrons, produced only within the bulk, set up a counter-field that tends to cancel the bulk field, E_2 , producing a voltage drop across the bulk that is less than would occur in a completely insulating medium; this is what is meant by the term screening. At sufficiently high intensities the counter-field approaches the bulk-field. Assuming the shielding occurs only in the bulk, the total voltage across the grain is now the sum of the voltage across the surface layers, which are equal but opposite in sign to that initially across the bulk.

Surface layers in barium titanate ceramic grains have been estimated at 10^{-6} cm (ref. 8). The remanent polarization typical of the ceramic material is about 8×10^{-2} C/m²; the relative dielectric constant of the poled ceramic is about 1300. We will estimate that the high-field dielectric constant is roughly one half the bulk dielectric constant. From equation (6) the bulk-field, for a typical 10^{-3} cm grain is,

$$E_2 = -0.35 \text{ V}$$

The saturation photo-emf would thus be 350 V/cm, or at least of that order of magnitude.

The potential across the surface layer is

$$\int_0^s E_1 dx + \int_0^s E_2 dx = (n_0 es) s$$

The saturation photo-emf and the polarization are therefore related linearly in the model, as is experimentally observed.

It should be noted that, as the temperature increases, not only is P_0 decreasing, but the dielectric constant, ϵ_s , is undoubtedly increasing. The saturation photo-emf might therefore be expected to decrease with temperature more rapidly than the remanent polarization. Such a behavior has been observed in BaTiO₃ + 5wt% CaTiO₃ ceramic (ref. 4).

CONCLUDING REMARKS

Summarized, our suggestion is that the emf's (and currents) arise from the presence of photoconductor-insulator sandwiches in the presence of space-charge-produced internal fields. The experimental results are in general agreement with the theory. Nevertheless, the model remains so

over-simplified that the possibility of the agreement being fortuitous is a reasonable one. Quite different explanations for high photo-emf's in ferroelectrics have been propounded by Johnson (ref. 10) and others in connection with studies of light-induced refractive index changes in lithium-niobate single crystals.

The experimental results are significant, however, when taken alone. They suggest a general phenomenon in ferroelectric ceramics, significant in magnitude and with unique characteristics. We not only have a consistent producer of high-voltage photoelectricity but a photo-battery, the polarity and magnitude of which can be switched by application of an electrical signal. It is also a phenomenon involving cheap polycrystalline materials. Certainly it warrants further investigation, especially from a materials point of view.

Acknowledgements — I would like to thank Frank Crowne and Harold Watkins of the Harry Diamond Laboratories who contributed in essential ways to this paper.

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**TABLE 1. – PHOTOVOLTAIC OUTPUTS AT WAVELENGTHS
PRODUCING MAXIMUM SHORT CIRCUIT CURRENTS**

Material	Illumination wavelength, nm	Photo-emf, V/cm	Photocurrent, $\mu\text{A/cm/W/cm}^2$
BaTiO ₃ + 5wt% CaTiO ₃	403	360	0.020
PLZT 7/65/35, polished	382	1500	0.030
PLZT 8/65/35, polished	382	750	0.015
Pb(Zr _{0.53} Ti _{0.47}) + 1wt% Nb ₂ O ₅ , unpolished	373	420	0.63
Pb(Zr _{0.53} Ti _{0.47}) + 1wt% Nb ₂ O ₅ , polished	373	510	1.0

**TABLE 2. PHOTO-emf FOR DIFFERENT GRAIN SIZE
(The material is PLZT 8/65/35.)**

Grain size, μ	Photo-emf, V
2-4	750
3-5	510
4-6	330
greater than 6	250

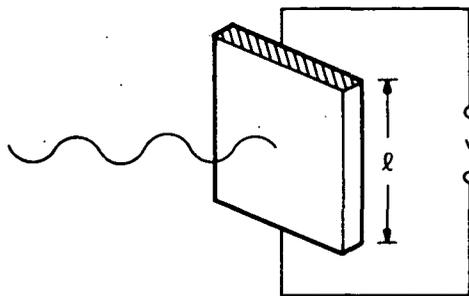


Figure 1.— Schematic of an illuminated sample.

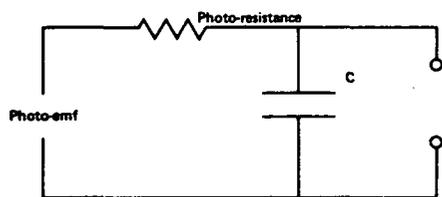


Figure 2.— The equivalent circuit of an illuminated sample. C is the sample capacitance.

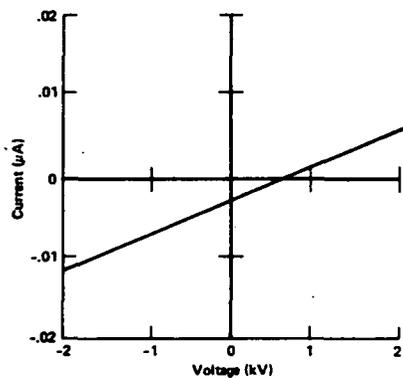


Figure 3.— Current vs applied voltage for an illuminated sample.

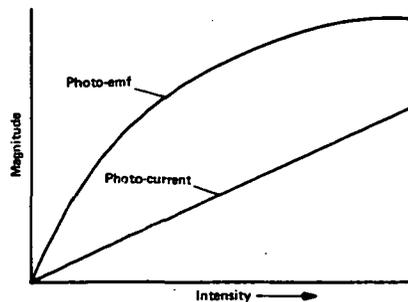


Figure 4.— Intensity dependence of photo-emf and photocurrent for a typical material.

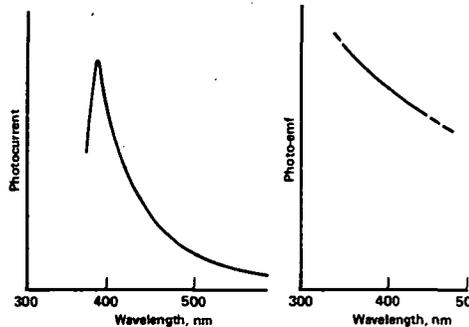


Figure 5.— Spectral behavior of photocurrent and photo-emf for $\text{Pb}(\text{Zr}_{.53}\text{Ti}_{.47})\text{O}_3 + 1\text{wt}\% \text{Nb}_2\text{O}_5$.

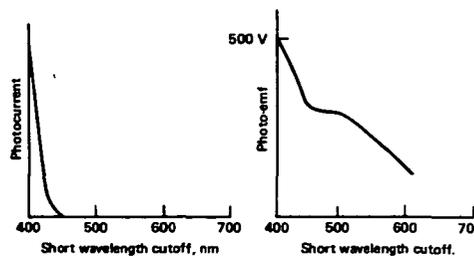


Figure 6.— Spectral dependence of photocurrent and photo-emf for $\text{Pb}(\text{Zr}_{.53}\text{Ti}_{.47})\text{O}_3 + 1\text{wt}\% \text{Nb}_2\text{O}_5$.

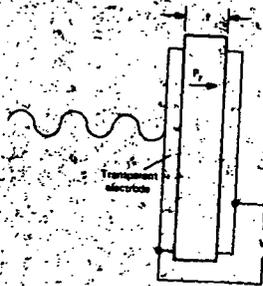


Figure 7.— Light incident through transparent electrode. P_r is the remanent polarization.

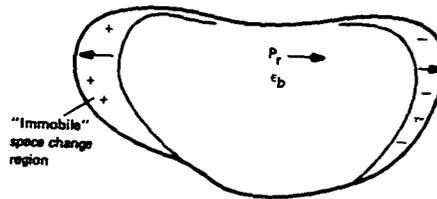


Figure 9.— Structure of a grain.

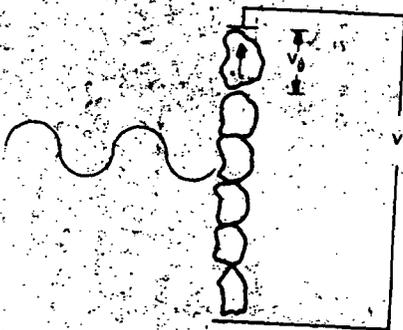


Figure 8.— Emf's across grains adding to produce a length dependent effect in a ceramic.

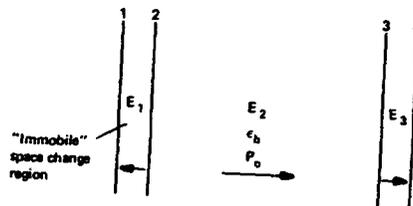


Figure 10.— 2-D model of a grain.

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DISCUSSION

Joe She, Colorado State University – Is there a phase transition temperature in these materials?

Philip Brody: Yes, the phase transition in barium titanate is at 120° . You have to operate below the phase transition which is at 465°C for the material which has the highest efficiency that I have examined so far. It drops linearly with the temperature, but the current goes up. With the PZT materials I've gone up to 120°C and the power is not dropping. That is, the current is going up with temperature while the voltage is going down.

Dick Stirn, J. P. L. – From the last slide, are you interpreting the high voltage as from one grain of material rather than a series effect?

Philip Brody: Well, the voltage appears across a grain but the high voltage is a series effect. Each grain only has about one-half volt across it. I've also looked at single crystal barium titanate and seen the order of one volt. However, I've just gotten some recent measurements in lead niobate which are producing about forty volts per centimeter in a true bulk effect.

Dick Stirn, J. P. L. – You recognize, of course, that the large series resistance of these materials will limit their usefulness for power conversion; even one tenth of an ohm will be a problem.

Philip Brody: Right, although it has not yet been examined at high laser intensities. Perhaps it will blow up before high currents are achieved. However, this is a new phenomena and it needs investigation. It seems that it would find its greatest use in production of high voltages at somewhat reduced powers.

Ned Razor, Razor Associates – I assume that you haven't made any estimates or projections of the energy conversion efficiency.

Philip Brody: I did the simplest thing you could do. I said what is the photon energy and how many volts is the electron dropping and it comes to 20 to 30 percent.

Ned Razor, Razor Associates – The problem comes, of course, whether you can deliver that at one volt and with a reasonable current density. My thought is that perhaps this device could operate in a periodic discharge mode. Since the capacitance is too great, what you are looking at is merely the sort of leakage, whereas if you charged and discharged on a periodic basis you could perhaps get around the impedance problem.

Philip Brody: Yes, that's true. We operate in the static or dc mode to separate this effect from pryolytic effects, however you could go in a charge-discharge mode to achieve large currents. The efficiency would not increase, however.

Max Garbuny, Westinghouse – Have you tried a Q-switched laser pulse on these materials?

Philip Brody: No, we have been so short of money that even the cost of \$2000 to replace a laser tube right now is holding up the research. In the future we hope to be able to.