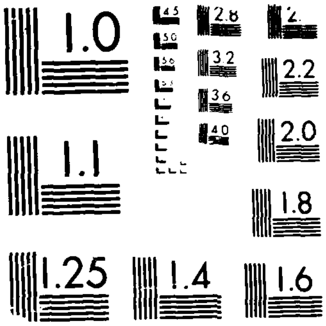
AD-A193 244   POLYMER-CERAMIC COMPOSITES(U) UNIVERSITY COLL OF NORTH   1/1
WALES BANGOR SCHOOL OF ELECTRONIC ENGINEERING SCIEN CE
D K DAS-GUPTA JUN 87 DAJA45-86-C-0034

UNCLASSIFIED   F/G 20/3   NL



MICROCOPY RESOLUTION TEST CHART

BUREAU [illegible] STANDARDS 1963 A

(2)

POLYMER-CERAMIC COMPOSITES

U.S. ARMY - ERO CONTRACT NO. DAJA45-86-C-0034

Third Interim Report

Principal Investigator: D.K. Das-Gupta,
School of Electronic Engineering Science,
University College of North Wales,
Dean Street,
Bangor, Gwynedd, LL57 1UT.
Telephone: (0248) 351151 Ext. 1696

June 1987

Abstract

Dielectric losses in a ceramic-polymer (PZT/PVDF) have been studied in the frequency range 10^{-4}Hz to 10^{-1}Hz from an analysis of the behaviour of the discharge currents. These results have been compared with the corresponding values of PVDF and PZT for which identical measurements, described above, were made. The results show again that even in the low frequency range of 10^{-4}Hz to 10^{-1}Hz the dielectric behaviour of the composite is dominated by that of the polymer (PVDF). However, the electrical conductivity of the composite is significantly similar to that of the ceramic (PZT).

Introduction

The first and second reports (combined) showed that the composite films of PZT/PVDF, prepared in our laboratories, may have a permittivity in excess of 100 for a 75% volume fraction of PZT powder introduced in the matrix of PVDF host polymer. The relative permittivity of the ceramic-polymer composites were measured in the frequency range of 10Hz-65kHz and compared with the respective permittivity values of PZT and PVDF. It was also observed that the dielectric relaxation of this PZT/PVDF composite conforms with that of the polymer (PVDF).

Present work exrtends above work to investigate the dielectric loss behaviour of the composite in the frequency range of 10^{-4} Hz - 10^{-1} Hz from a study of the absorption current behaviour. It also provides an analysis of possible ionic conduction in PZT/PVDF composite.

Experimental

PZT powder with an average grain particle size of 20μm was purchased from Unilator Technical Ceramics of Ruabon, Great Britain. Pellets of PVDF were kindly supplied by Laporte Industries of Luton, England. They were mixed in various concentrations using a rolling mill operated at 160^{o}C. The composite hides were then pressed in a temperature-controlled hydraulic press to thicknesses in the range 100 to 800 micron. The use of high quality chromium plates for pressing allowed the production of films with a good surface texture. Samples were thoroughly cleaned with ethyl alcohol in an ultrasonic bath to remove all surface contaminants. They were then annealed in an oven for 72 hours at 80^{o}c to condition them. These processes were found to improve repeatability and increased both bulk and surface breakdown strengths.

In order to perform dielectric and conduction measurements, samples were furnished with circular electrodes of aluminium of 0.1μm thickness and 24mm diameter by vacuum evaporation. Some tests were also performed with gold electrodes but no variation was found. We were also kindly supplied with discs of PZT by Unilator which were already furnished with fired silver electrodes of 2μm thickness.

Experimental measurements were all performed in a stainless steel vacuum chamber at a pressure $<10^{-5}$ Torr. Temperature control to within 0.25 degrees was established by Eurotherm controller. High voltage was applied to samples from a Brandenburg Photomultiplier Supply and currents were measured with a Keithly (Model 616) Digital Electrometer suitably interfaced to a microcomputer (Acorn BBC) which stored data, plotted curves and performed transformations 'on-line'.

The samples produced by milling and pressing tended to be brittle when the PZT proportion was high (>60% by volume). This could lead to great difficulties when thin films are required, especially if the dielectric is required to conform to some curved or otherwise complicated surface. A possible solution to this problem is the incorporation of a third material in the composite in order to provide increased flexibility. A fluoro-elastomer may have the necessary properties for this application but a plasticizer may be easier to incorporate into the matrix of the type employed here.

We have investigated the use of plasticized samples in a limited manner. We first partially dissolved PVDF pellets in a warm mixture of methyl sulphoxide and dimethyl formamide solvents to which measured quantities of triotyl phosphate and dioctyl phthalate plasticizers were added. On cooling a suspension of PVDF was obtained which could easily be mixed with PZT powder to form a composite. The mixtures were allowed to dry slowly in a flow of moist nitrogen and were then pressed into thin films (100μm thickness) at room temperature. They were then vacuum dried for 24 hours to remove all traces of solvent before being conditioned at 60°c to improve texture. Films were electroded and their characteristics measured in the manner described above.

Results and Discussion

Typical charging and discharging transients for PZT and a composite sample with a high PZT content (75%) are shown in Figure 1. It may be observed that at 333K and for a low field of 0.16MV/m a steady state conduction current is achieved within 1000 seconds. Similar behaviour was found at all temperatures above 313K and for the range of fields investigated in the present work. The charging currents for the composite material may be observed to decrease monotonically with time for at least 10000 seconds.

Figure 2 shows similar data for pure PVDF and for a composite sample containing equal volumes of PVDF and PZT. The charging currents are lowest in the case of PVDF and it may be observed that the current after 10000 seconds increases as the proportion of PZT is increased.

The discharge currents observed when the applied field was removed, were opposite in polarity to the charging currents in all cases and were smaller in magnitude. This suggests that the dominant mechanism responsible for such currents was dipolar reorientation. In all cases except for pure PZT, the transient current dominated the conduction current.

The discharging current transients may be transformed into the relevant low frequency dielectric loss information using Fourier Analysis or by the Hamon approximation[1]. The loss factor " at frequency, f, is related to the discharge current, I_d, at t seconds following the removal of the field E (=V/d), where V is the voltage and d the thickness, by the equation:

$$\varepsilon''(f) = \frac{I_d(t)}{2\ fC_aV} = \frac{I_d(0.1/f)}{2\pi f(C_aV)} \qquad \ldots (1)$$

Where C_a is the geometric capacitance of the electrode assembly without the sample, V the magnitude of the step voltage and f is the Hamon frequency, given by:

$$f = 0.1/t \qquad \ldots (2)$$

The approximation is only valid provided that the charging time exceeds the recorded discharging time by about an order of magnitude. In the present work the charging time was 10000 seconds which allows us to transform discharging data up to 1000 seconds and provide low frequency loss information to frequencies as low as 10^{-4} Hz.

Low-frequency loss spectra for PZT, PVDF and a 50% composite sample are shown in Figure 3 in which the loss factors for PVDF and for the composite sample have been multiplied by a factor of 10 in order to improve clarity. A peak may be observed for PZT in the vicinity of 1mHz and with a magnitude of

90. This may be due either to ionic impurities, or the motion of protons, or the presence of electronic space charge which may be trapped at domain walls. This last possibility may be quite likely in a ferroelectric material such as PZT which is highly polar. No peak may be observed in the other materials but it is likely that the loss process does peak at this temperature but at a lower frequency and outside the range investigated in the present work. This is consistent with our earlier work in which we observed the α_i relaxation in PVDF at 0.1mHz at 353K. The similarity between the low frequency behaviour of the composite material and that of pure PVDF suggests that the polymer properties dominate the dielectric behaviour of the polymer.

We have shown elsewhere[2] that the conduction process in PVDF at high temperatures and at high fields is best described by an ionic model with an average jump distance of 2.5nm. The electrical conduction in a crystalline ceramic such as PZT is also ionic and it would appear likely that the conduction in a composite of these materials would also be ionic. We have investigated this behaviour by analysing the field dependence of the conduction current both in PZT and in a composite and the ionic conduction plots are presented in Figures 4 and 5 respectively.

According to Lawson[3], the high field dependence of the ionic conduction current, I_s, is given by an expression of the form:

$$I_s(T) = I_o(T) \exp(ejE/2kT) \quad \ldots (3)$$

where I_o is a temperature dependent constant incorporating the thermal activation energy, e is the electronic charge, j is the jump distance and k is Boltzmann's constant. Hence, plots of log (I_s) vs E or voltage should yield straight lines from which the average jump distance may be evaluated. From the gradients of Figures 4 and 5 the average jump distances in PZT and in the composite were calculated to be 46 and 43nm respectively with an uncertainty of 5nm. These results seem to indicate that the role of PZT is dominant in the conductivity of the composite. However, the analysis given above should be treated with some caution as the range of fields employed may not extend to a sufficiently high level to ensure that an ionic mechanism operates. Indeed, the deviation form ohmic behaviour was observed to be only slight in the case of PZT. In the present work we have deliberately not considered alternative models such as the Schottky effect and Poole-Frenkel conduction as these may not be appropriate in polymer systems below fields of the order of 10MV/m. It may, of course, be necessary to consider such processes with the thinner films which may be appropriate to capacitor systems.

Conclusions

We have prepared composite materials by combining a high permittivity ceramic with a thermo-plastic. The resulting samples can be processed adequately with simple apparatus but tend to become brittle when the ceramic content is high. The addition of plasticiser or elastomer improves mechanical characteristics without decreasing electrical strength. Relative permittivities of the order of 100 can be obtaineed with these materials providing that the dielectric constant of the polymer is sufficiently high. Although the electrical conductivity of the composite is govermed by the ceramic the dielectric properties are similar to those of the polymer.

Further work is in progress to evaluate the pyroelectric coefficients of the PZT/PVDF composites.

References

1. B.V. Hamon: Proc. IEE; 99 (1980) 151.
2. D.K. Das-Gupta, K. Doughty & R.S. Brockley: J. Phys. D; 13, (1980) 2101.
3. W.G. Lawson: Br. J. Appl. Phys.; 16, (1965) 1805.

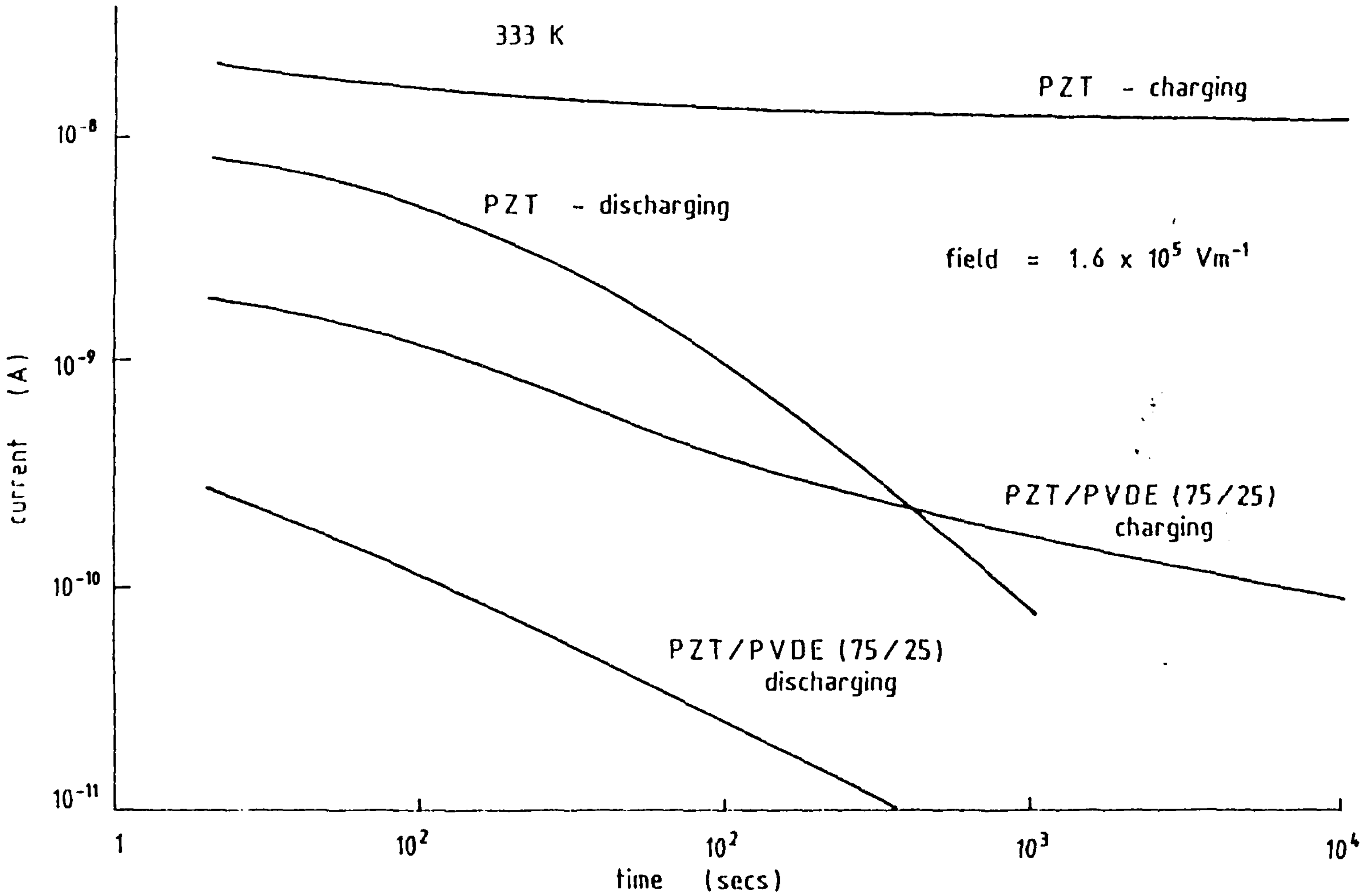


Figure 1: Charging and discharging current transients in PZT and in a 75% PZT composite at 333K.

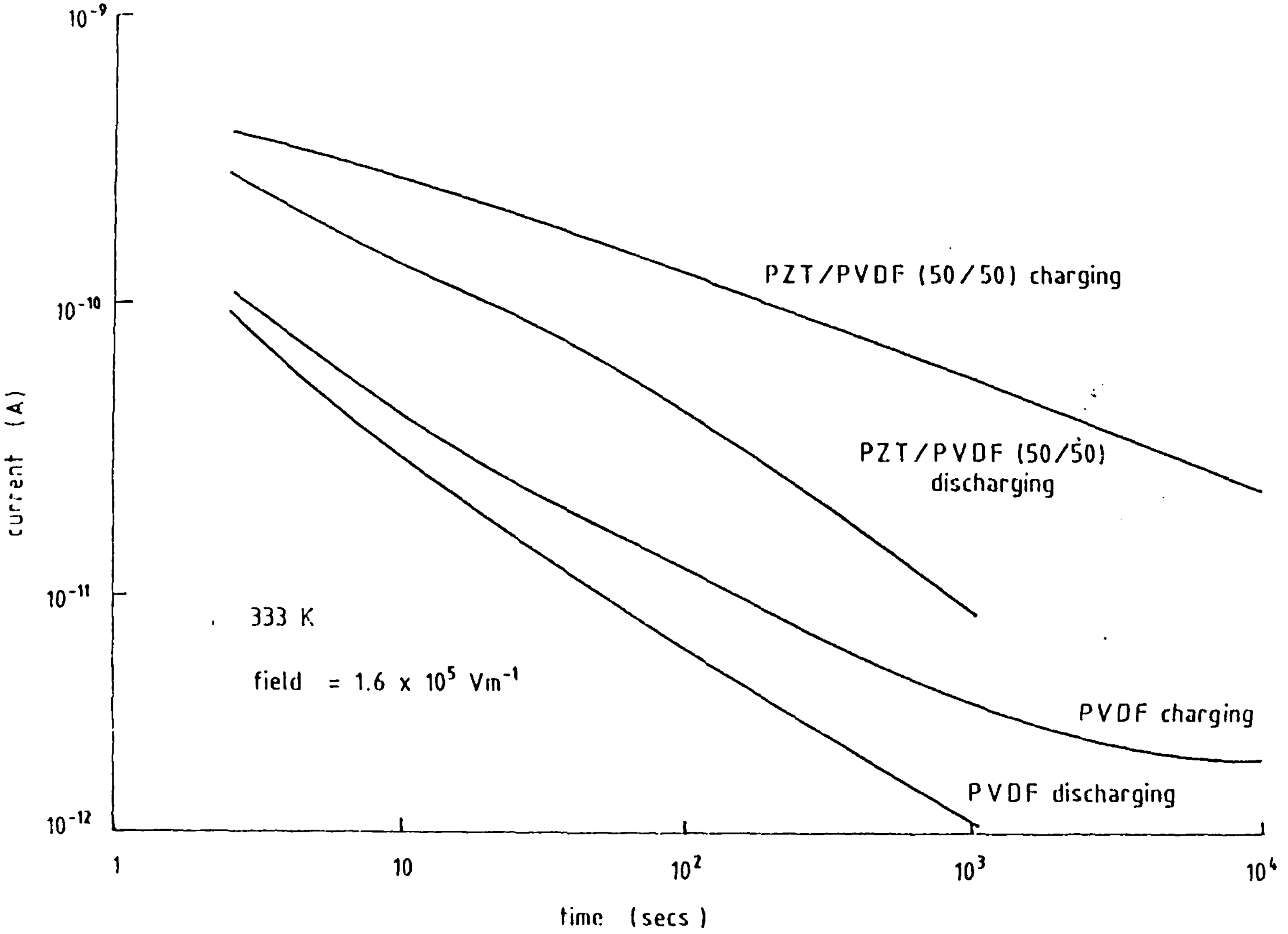


Figure 2: Charging and discharging current transients in PVDF and in a 50% PVDF composite at 333K.

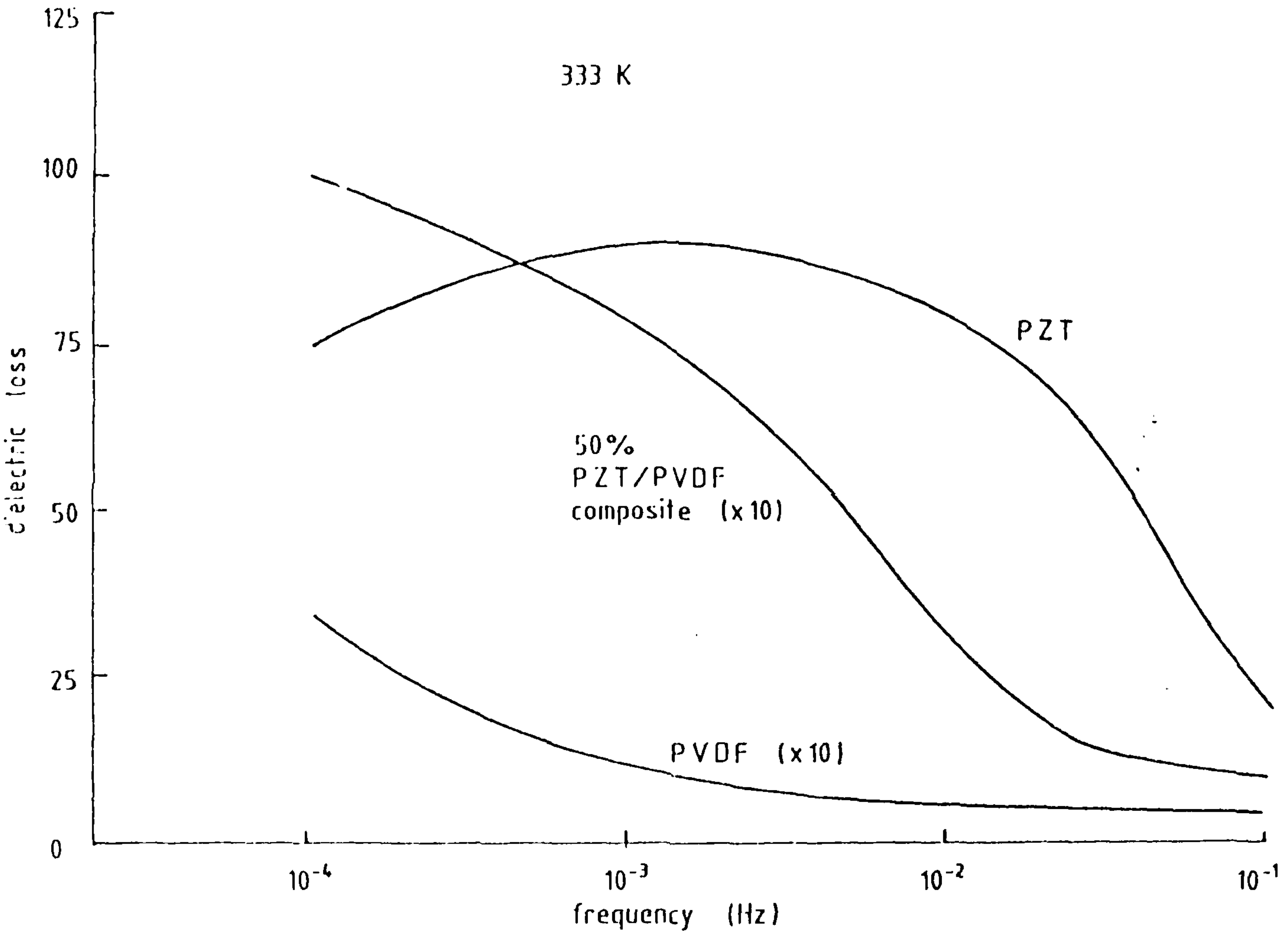


Figure 3: Low frequency dielectric loss spectra in PZT, PVDF and composite at 333K by Hamon approximation.

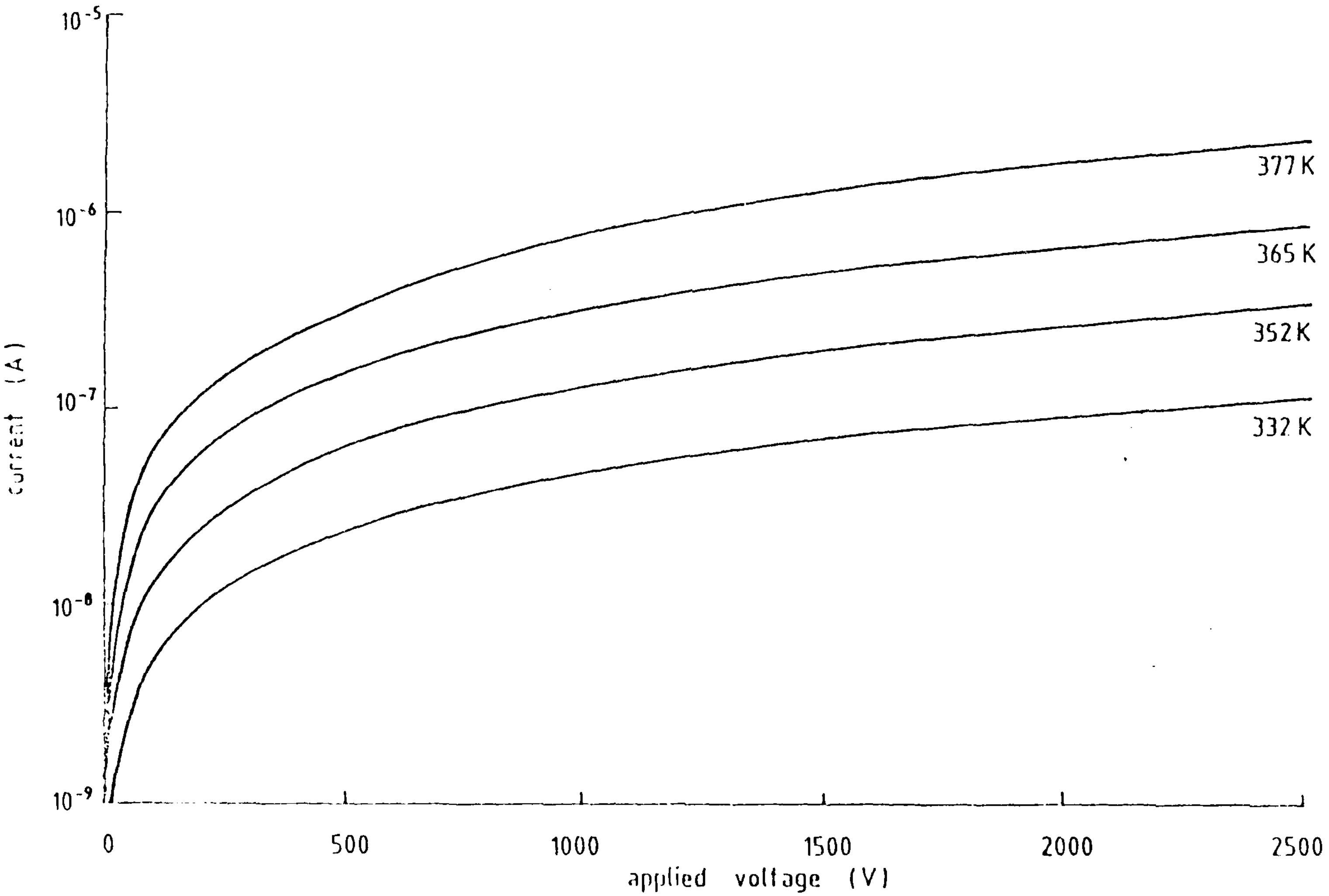


Figure 4: Ionic conduction plot in P ZT.

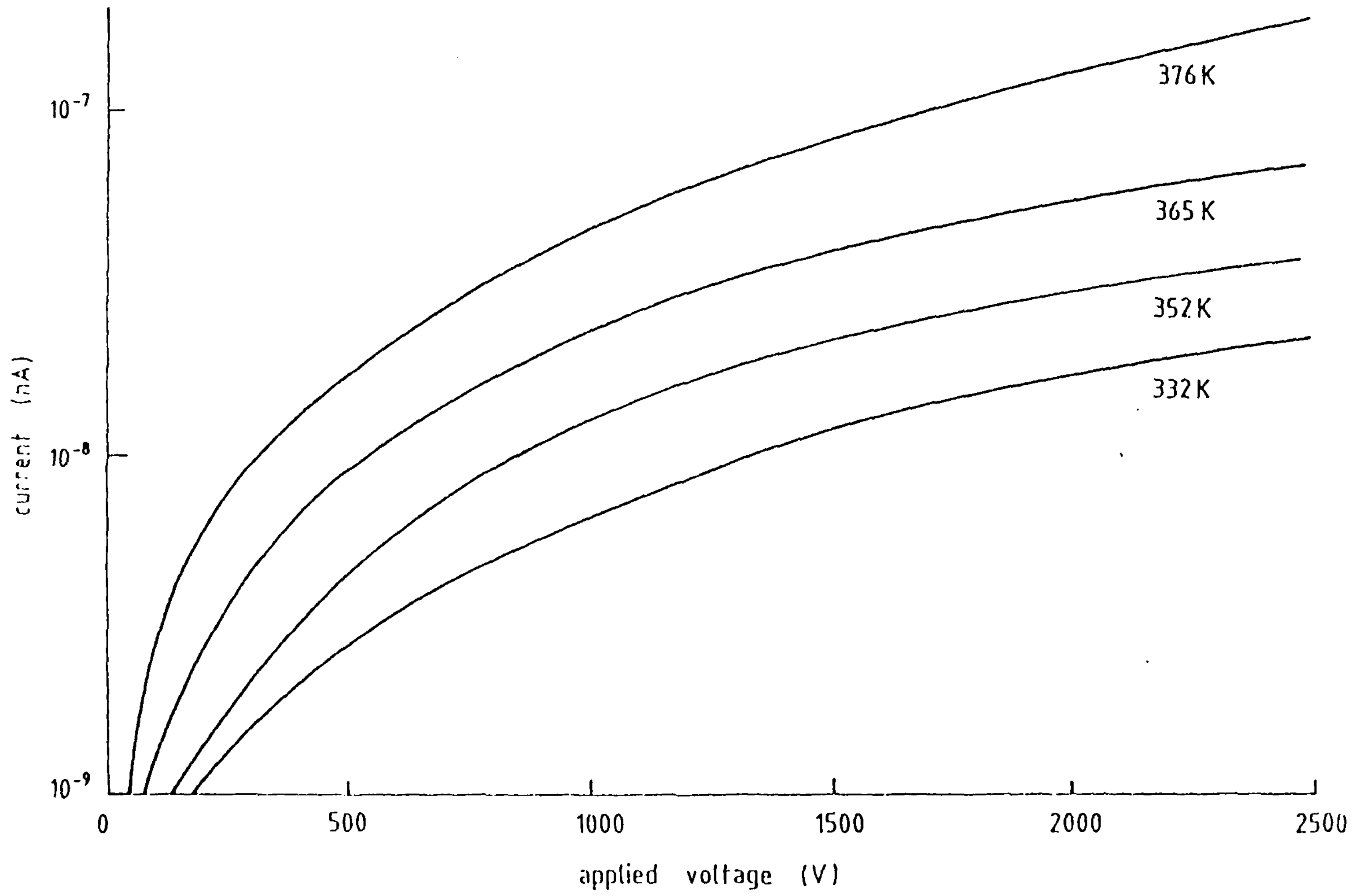


Figure 5: Ionic conduction plot for PZT/PVDF composite.

END
DATE
FILMED
DTIC
JULY 88