ARMY RESEARCH LABORATORY

Analysis of Ferroelectric Thin Films Grown by MOD Process

by Robert Hoffman and Wesley Tipton

ARL-MR-375

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Analysis of Ferroelectric Thin Films Grown by MOD Process

Robert Hoffman and Wesley Tipton
Sensors and Electron Devices Directorate

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3701 N. Fairfax Drive
Arlington, VA 22203

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Abstract

The Army Research Laboratory (ARL) has performed ferroelectric characterization testing of thin film ferroelectric samples provided by Raytheon TI Systems (RTIS) for the DARPA (Defense Advanced Research Projects Agency) uncooled detector materials program. The samples measured at ARL, produced by the metal-organic decomposition (MOD) method, have hysteresis loop characteristics, remanant polarization, and dielectric constant and resistivity values commensurate with measurements made at RTIS. RTIS projections show that Ca- and Sn-doped samples should achieve a projected noise equivalent temperature difference (NETD) of 13.8 mK with 48.5-μm pixels and 26.5 mK with 50-μm pixels, respectively.

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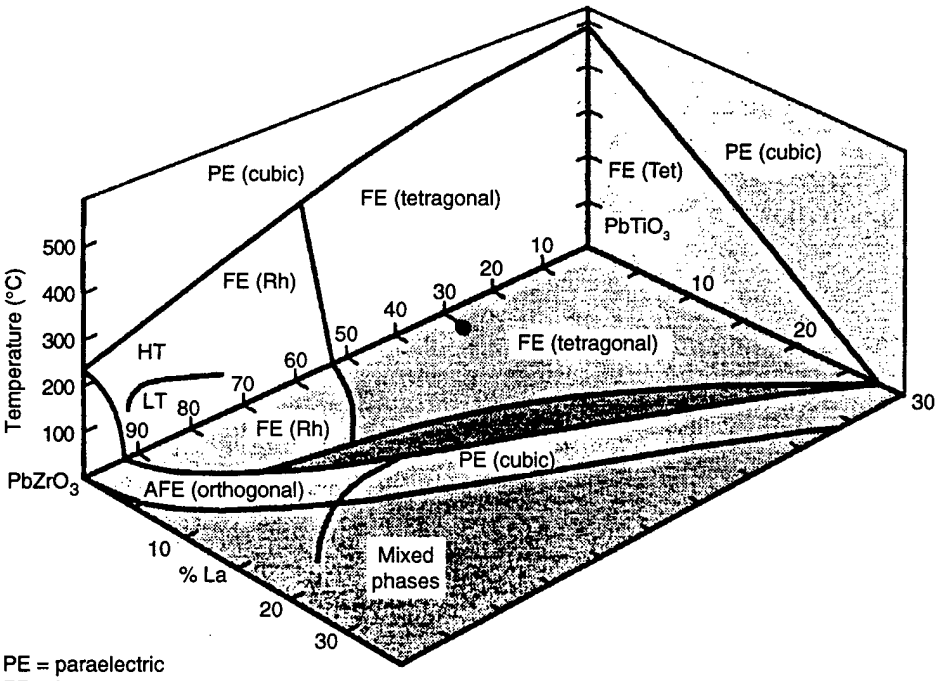
1. Introduction

The Army Research Laboratory (ARL) has performed ferroelectric characterization testing of thin film ferroelectric samples provided by Raytheon TI Systems (RTIS). ARL has endeavored to create state-of-the-art ferroelectric testing facilities in-house in order to provide an independent system of verification of the ferroelectric thin film materials produced under a contract with RTIS. Specifically described here are hysteresis loop measurements made at ARL. Remanant polarization, dielectric constant, and resistivity data are derived from the hysteresis loop data.

2. Sample Fabrication

The samples sent by RTIS were a part of a study to determine the effects of lead nonstoichiometry and electrode configuration on the ferroelectric characteristics of the films. The composition of the lead lanthanum zirconium titanate (PLZT) films in all cases was (3/30/70), meaning the mole fraction was 0.03 for lanthanum, 0.3 for zirconium, and 0.7 for titanium. The lead concentration was enhanced in each case by 10 mol % to compensate for lead loss during annealing. Figure 1 shows a phase diagram showing the various ferroelectric, antiferroelectric, and paraelectric phases with respect to composition. The dot at 3 mol % La, 30 mol % Zr, and 70 mol % Ti is within the tetragonal ferroelectric phase region of the phase diagram.

Figure 1. Room temperature PLZT phase diagram.



PE = paraelectric
FE = ferroelectric
AFE = antiferroelectric
HT = high temperature
LT = low temperature
Rh = rhombohedral

The samples were made by the metal-organic decomposition (MOD) method, which has proven to be a very economical and efficient method of producing high-quality thin films of ferroelectric materials. MOD involves the deposition on a rotating substrate of a solution of the various component ions of the material. Typically, acetates or acetate derivatives of the metal ions are dissolved in an aqueous or alcohol solution in the correct stoichiometric proportions. The solution is dispensed onto a substrate rotating at several thousand revolutions per minute. Upon contact, the solution evaporates, leaving an amorphous film of the acetates. Pyrolyzing at several hundred degrees Celsius removes most of the organic residue. Calcining at higher temperatures oxidizes away the residual carbon and crystallizes the ferroelectric in the perovskite phase.

All the samples produced under this contract were annealed in a rapid thermal annealer (RTA). The principal differences in these particular samples are in the ferroelectric film thickness, the lead stoichiometry, and the top/bottom electrode thickness (and manner of deposition). The samples were provided with a bottom contact and with square top contact pads of varying sizes, from 0.25 mm on a side to 1.0 mm on a side (fig. 2).

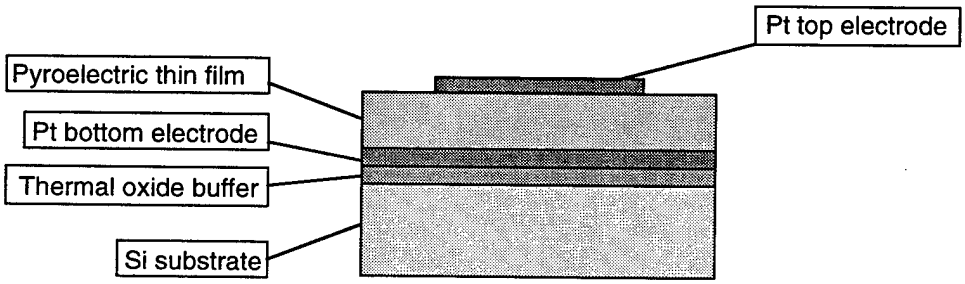


Figure 2. Film structure of MOD deposited capacitors.

3. Hysteresis Loop and Loss Tangent Measurements

We performed the hysteresis loop measurements with a Radiant Technologies RT-66A ferroelectric measurement system. We used a Wentworth probe station equipped with a stereo microscope to make electrical contact to the sample. The data were acquired with the software supplied with the RT-66A on a standard 386 PC. The RT-66A system is capable of applying up to 40 V peak-to-peak voltage to the sample. The RT-66A provides complete sample information such as P_s (saturation polarization, $\mu C/cm^2$), P_r (remanant polarization, $\mu C/cm^2$), V_c (coercive field, V), ε_r (relative dielectric constant), and R_y (resistivity, Ω cm). The loss tangent data were obtained as a function of frequency from 100 Hz to 1 MHz by a Hewlett-Packard HP4194A impedance analyzer. RTIS did not specify at what frequency their tan δ measurements were taken; however, at 100 Hz, tan δ is at a minimum in all cases observed, so all ARL measurements were made at 100 Hz. Although the measurements are not a complete or definitive diagnostic of ferroelectric thin film performance, they provide a needed guidepost to gauge progress in thin film ferroelectric development. Table 1 summarizes both the RTIS data and the ARL data. Table 2 summarizes the film structure and annealing treatments (where available) of each film.

Table 1. Summary of hysteresis loop measurements.

Data	Sample ID	ε_r	tan δ	P_s ($\mu C/cm^2$)	P_r ($\mu C/cm^2$)	V_c (V)	R_y (Ω cm)
RTIS	161	490	0.04	34	11	2.3–3	10^{10}–10^{11}
ARL	161	341	0.05	34.6	8.6	3.3	1.7×10^{10}
RTIS	163	530	0.013	25–34	11–15	4.7	10^{10}–10^{11}
ARL	163	202	0.016	31.0	11.0	4.3	5.1×10^{11}
RTIS	170	320	0.013	26	11	4.5	10^{10}
ARL	170	200	0.026	17.1	1.99	0.4	3.1×10^{11}
ARL	170	268	—	6.1	5.1	–8.0	1.1×10^{12}
RTIS	164	410	0.030	19–28	6–10	3.7	10^{6}–10^{11}
ARL	164	403	0.010	26.1	14.1	1.4	1.6×10^{3}
ARL	030	1013	0.026	27.4	7.8	5.7	1.5×10^{11}
RTIS	results not available						
ARL	280	859	0.028	24.2	5.1	2.5	1.3×10^{8}
RTIS	results not available						
ARL	137	404	0.029	33.1	9.6	4.3	4.1×10^{10}
RTIS	results not available						

Table 2. Summary of film structure and treatment.

Sample ID	Film thickness (Å)	Ti/Pt bottom electrode	Top electrode	Anneal schedule
161	1500	CRL	Pt (Hum)	600/10 s
163	1500	CRL	Ti/Pt (Hum)	600/10 s
164	1500	CRL	Ti/Pt (Tem)	600/10 s
170	3000	Tem	Pt (Hum)	600/30 s

Tem = Temescal deposition unit
CRL = RTIS Corporate Research Laboratory deposition facility
Hum = Hummer sputter deposition unit

4. Test Results

The ARL data represent data taken on a single pad, or in the case of sample 170, two pads on the same sample. The ARL data closely track the RTIS data except for the relative dielectric constant ε_r, for which we consistently found lower measurements. We believe that sample 170 was thermally compromised before it was sent to ARL, which would explain the dielectric anomalies observed and its crazed appearance.

Several anomalies appear in the hysteresis loop data as well. For example, in sample 163 the hysteresis loop is discontinuous, as it is with samples 170, 164, 280, and 137. In samples 163, 164, 280, 137, and PBT-20 (fig. 3), it appears that there are two values for the remanant polarization on the negative part of the loop. This phenomenon, known as imprinting, results when the film has a preferred polarization at zero applied field. Most likely, imprinting is due to ferroelectric domains that are "pinned" in the film because of strain induced during deposition and annealing. One pad of sample 170 exhibits even more unusual behavior. The loop is decidedly asymmetric, yielding a V_c that is negative (fig. 4), possibly due to thermal damage. The other pad of sample 170 investigated yields a curve that is generally symmetric, but the shape resembles that of an antiferroelectric material, with two almost separate loops seen in the positive and negative quadrants. The behavior of sample 161 appears normal in most respects, except that almost 40 V of peak-to-peak voltage is required to obtain the hysteresis loop. This voltage seems excessive compared to those required for other films grown at other facilities. For example, sample PZT 102491B-1, a thin film of lead zirconium titanate (PZT) shown in figure 5, exhibits the expected behavior of a thin film ferroelectric material. This film exhibits symmetric behavior and saturates at only 20 V peak-to-peak. A "typical" RTIS hysteresis loop is shown in figure 6. As reported by RTIS, the only difference in the supplied samples lies in the electrode systems and the heating schedule used to anneal the film. It would appear that the heating schedule used to anneal sample 170 has thermally damaged the film. In addition, the relatively flat tan δ versus frequency performance of this film from 100 Hz to 1 MHz suggests that it is behaving more like a lossy dielectric than a ferroelectric material.

Figure 3. Hysteresis loop of RTIS sample PBT-20 with imprinting.

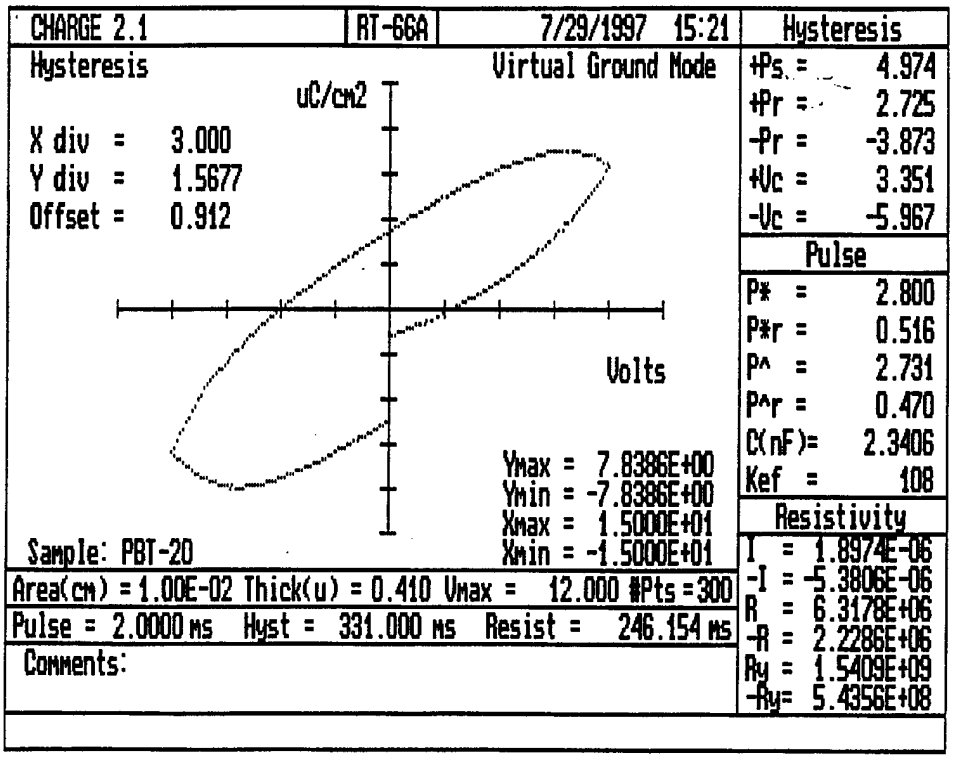


Figure 4. Hysteresis loop of RTIS sample FET 170 showing effect of thermal damage.

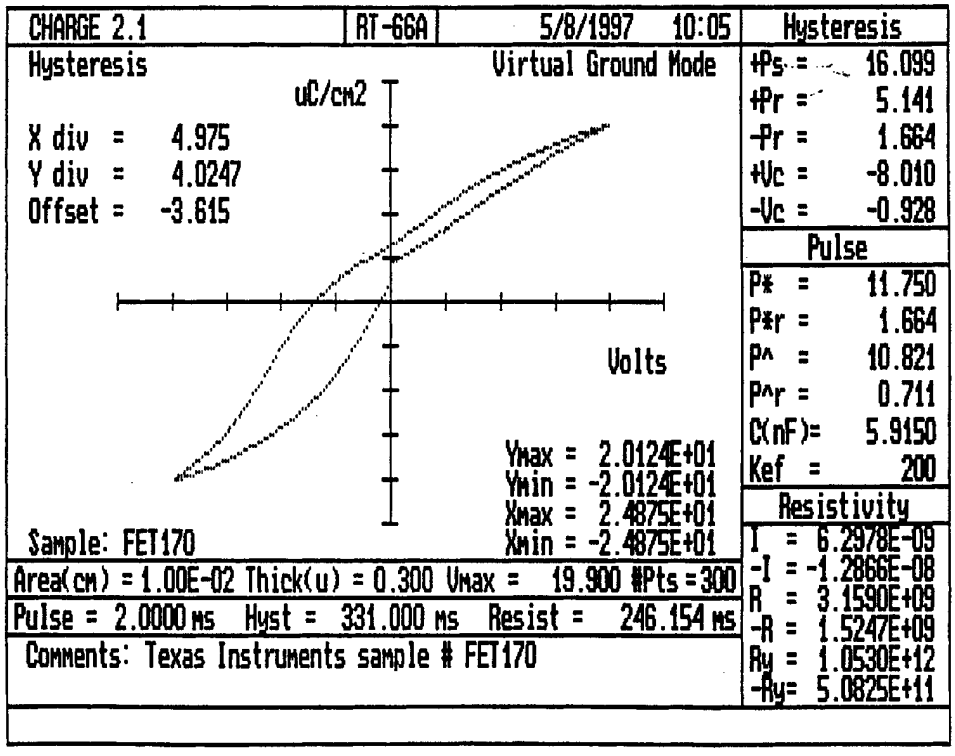


Figure 5. "Ideal" hysteresis loop of ARL sample.

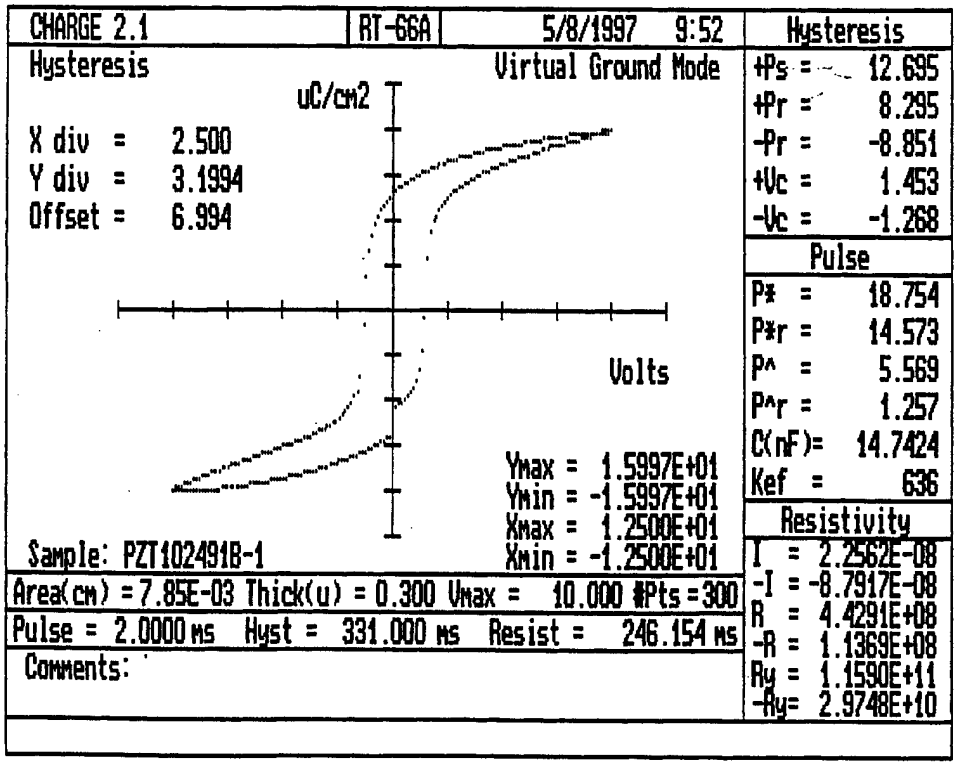
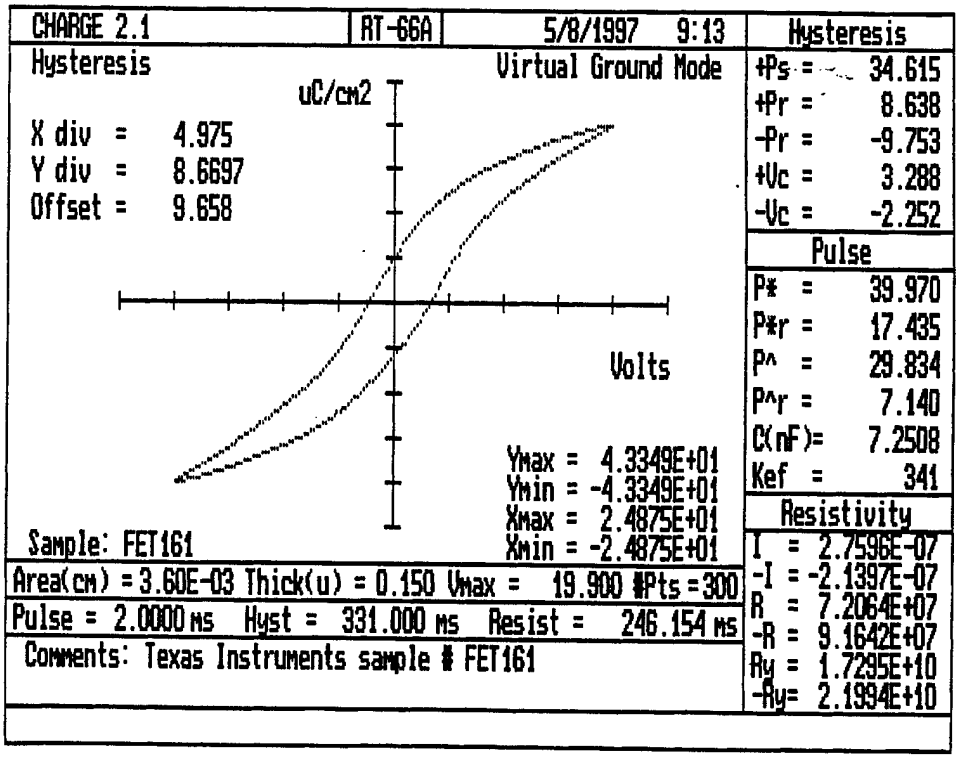


Figure 6. Hysteresis loop of typical RTIS sample (sample FET 161).



The very low resistivities of samples 164 and 280 most certainly lie in the large excess of lead in these samples. Both of these samples had concentrations of lead 20 percent above stoichiometry. All the rest had 10-percent excess lead above stoichiometry. Clearly, 20-percent excess lead has a deleterious effect on film performance, where 10-percent excess yields films with good properties. Films 164 and 280 also yielded hysteresis loops that saturated at more typical voltages (20 to 24 V peak-to-peak), rather than the 40 V peak-to-peak observed in the other samples. Some of the pads on both these samples leaked current so badly that they were visibly damaged by the current passing through them.

RTIS has also experimented with more complex substituted PLZT systems. Substitutions of Ca or Ba in the A-site in the perovskite structure, in place of Pb, result in marked improvements in material performance. Likewise, substitution of Sn in the B-site, in place of Ti, also results in further improved performance. A typical hysteresis loop of one of these films is shown in figure 7. Substantial decreases in the dissipation factor and the dielectric constant have been observed when Ba or Ca is substituted in the A-site (table 3). Increasing Ba from 10 to 20 mol % results in a decrease in ε_r from 140 to 110, and tan δ decreases from 0.016 to 0.010. Substitution of Ca in the A-site lowered ε_r from 89 to 80 and tan δ actually increased somewhat from 0.007 to 0.026. Double substitution of Ca in site A and Sn in site B allows for even greater improvement in the properties. A 10%Ca/10%Sn substitution maintained a low ε_r of 79 and a tan δ of about 0.012. However, there was a marked improvement in the pyroelectric coefficient p up to about 24 nC/cm^2-K. This corresponds to a noise equivalent temperature difference (NETD) of about 15 mK for a 48.5-μm pixel and 28.6 mK for a 25-μm pixel. A 20%Ca/10%Sn substitution also maintains ε_r and tan δ at 103 and 0.009, respectively, corresponding to an NETD of 13.8 mK for a 48.5-μm pixel and 26.5 mK for a 25-μm pixel.

We also investigated the effect of multiple cycles on the shape of the hysteresis loop and the dielectric measurements obtained. Measurements taken at 9 V yielded the smaller loop in figure 8. Increasing the voltage to 12 V yielded the larger loops in figure 8. This family of loops was created by three successive cycles of the instrument, and shows that the film changes characteristics with each successive cycle. The same measurement done at 9 V showed no such differences. Therefore, it would appear that the film is degraded when subjected to higher voltages during cycling.

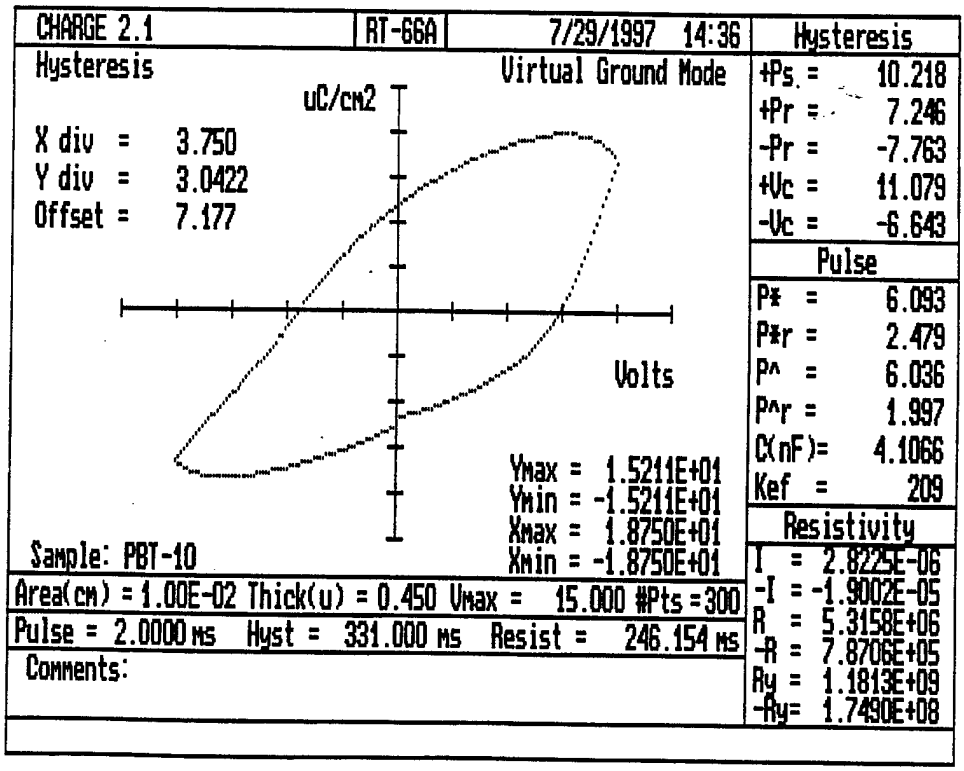


Figure 7. RTIS sample PBT-10 showing asymmetric hysteresis loop.

Table 3. Electrical properties of substituted lead titanates.

Sample	Thickness (μm)	ε_r	tan δ	p (nC/cm²-K)	Figure of merit ($\times 10^5$ Pa$^{-1/2}$)	Projected NETD (mK)	
						48.5 μm	25 μm
PBT-10	0.25	140	0.016	19.5	1.62	21.7	41.5
PBT-20	0.38	110	0.01	14.5	1.72	22.3	46.7
PCT-10	0.43	89	0.007	14.3	2.26	23.4	41.9
PCT-30	0.46	80	0.026	16.6	1.43	26.9	50.8
PCSnT-10/10	0.37	79	0.012	23.5	3.00	15.0	28.6
PCSnT-20/10	0.31	103	0.009	26.7	3.45	13.8	26.5

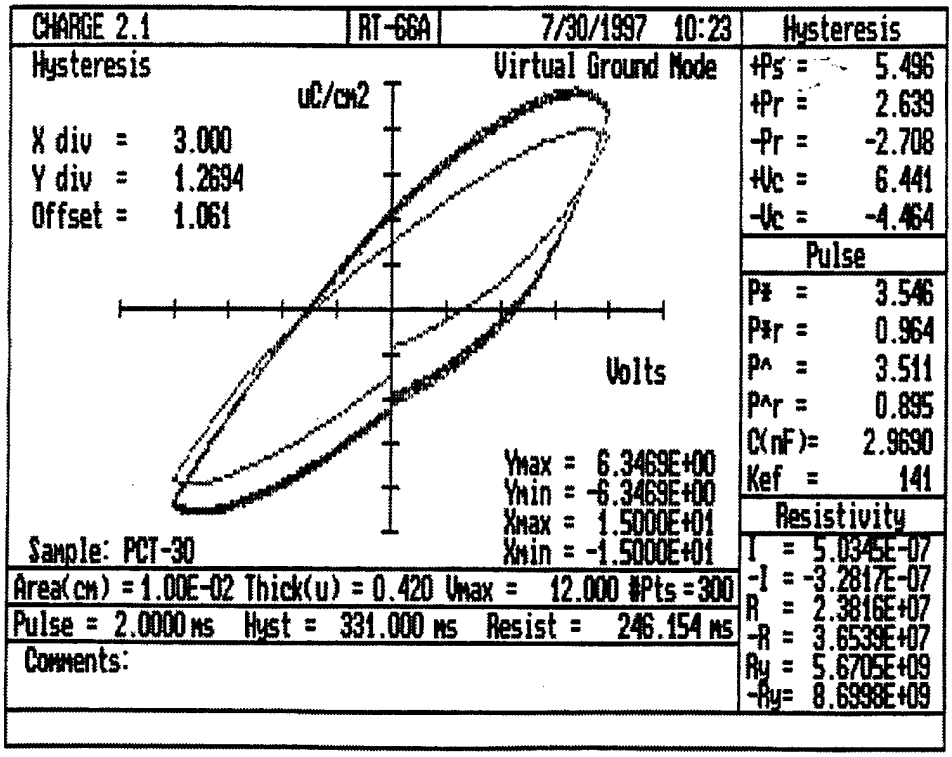


Figure 8. Hysteresis loop of RTIS sample PCT-30 showing effect of multiple cycles.

5. Conclusions

At this time, we do not know what the complete ramifications of the anomalies are for device performance. However, in the sensor array, the thin film will be poled to maximize the pyroelectric current generated, and any asymmetry or imprinting in the hysteresis loop should not adversely affect overall array performance. RTIS maintains that the consistently high pyroelectric coefficients measured readily offset the unusual behavior observed in the hysteresis data. Once poled, the film essentially will be maintained at that particular point in the hysteresis loop indefinitely.

With regard to the dielectric constant ($\varepsilon < 500$), the first-year goals have been met or exceeded. However, in most cases, the loss tangent is higher than the goal ($\tan \delta > 0.02$), although some of the samples exceeded the first-year goal. It is best to keep in mind that the samples tested for this report may not be wholly representative of the entire sample set. It also appears that the electrode system that RTIS used and its manner of deposition is crucial to device performance as well, but the largest changes and anomalies occurred when the lead was increased from 10 percent above stoichiometry to 20 percent.

RTIS is steadily approaching the 10-mK goal, having achieved 13.8 mK for 48.5-μm pixels, and 26.5 mK for 50-μm pixels. With continuing improvements in materials and processing, we are reasonably confident that RTIS will reach the 10-mK performance goal at the end of the three-year contract period.

In the near future we will test these samples to measure the pyroelectric coefficient of the samples supplied by RTIS. This test will enable ARL to independently calculate figures of merit and the NETD of samples produced under contract, as well as to evaluate samples of new materials grown in-house.

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DARPA
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Austin TX 78712

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U.S. Army Research Laboratory
Attn: AMSRL-SE-EP (e-mail: bhoffman@arl.mil)
2800 Powder Mill Road
Adelphi, MD 20783-1197

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