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Protocol for the Calculation of the
Dielectric Constant and Piezoelectric Coefficients
For Piezoelectric Single Crystals,
Including A Measurements Discussion
Version Date: July 25, 2001

OUTLINE

**Protocol for the Calculation of the
Dielectric Constant and Piezoelectric Coefficients
For Electroactive Single Crystals,
Including A Measurements Discussion**

1. EXISTING STANDARDIZED METHODS FOR MEASUREMENT AND CALCULATION OF THE SMALL SIGNAL DIELECTRIC CONSTANT AND THE PIEZOELECTRIC COEFFICIENT

1(a) The small signal dielectic constant and loss tangent can be measured using the technique described in ASTM Standard D 150-74 "A-C Loss Characteristics and Dielectric Constant (Permittivity) of Solid Electrical Insulating Materials".

1(b) The small signal piezoelectric coefficient can be calculated from the resonance measurement technique described in ANSI/IEEE Standard 176-1987 "IEEE Standard on Piezoelectricity". Resonance for these materials will be in the kHz to MHz range, depending upon available IEEE sample sizes and sample composition. If the material is not frequency dispersive (its T_{max} changes by less than 5^oC across three decades of frequency) then the value calculated represents the small signal piezoelectric coefficient over a wide frequency range. However, if the material is dispersive with frequency then the value calculated represents the small signal piezoelectric coefficient at the measurement frequency and temperature only.

1(c) In general, given the stress sensitivity of many of the single crystal compounds, it is not clear that accurate data can be obtained by Berlincourt or charge measurements as a function of applied stress, unless some guarantee is available that the measurement technique itself has not perturbed the domain state of the sample.

2. DEFINITION OF THE VARIOUS DIELECTRIC CONSTANT AND THE PIEZOELECTRIC COEFFICIENT CALCULATIONS COVERED BY THIS PROTOCOL

2(a) This protocol covers the calculation of the dielectric constant from a polarization versus electric field curve and the calculation of the piezoelectric coefficient from the strain versus electric field curve. The protocol covers the calculation of both small and large signal values from large signal measurements for these two material properties. It is not recommended that small signal values of the dielectric constant or the piezoelectric coefficient be calculated from small signal polarization or strain versus electric field curves produced on experimental setups designed for large signal measurements. Many experimental setups designed for large signal measurements will not have the resolution required for making accurate small signal measurements. Thus, the protocol does not discuss the calculation of small signal material properties from small signal measurements, however these small signal values are defined in this section.

2(b) For the purposes of this protocol small signal measurements are measurements in which the peak electric field does not exceed 0.01 MV/m.

2(c) For the purposes of this protocol large signal measurements are measurements in which the peak electric field is greater than 0.01 MV/m. Typically, large signal measurements are performed at peak electric fields of 0.5 MV/m and above.

2(d) Depending upon the response of the material and upon which calculations are to be made and reported it may be necessary to measure, calculate and report more than one dielectric constant or piezoelectric coefficient. These reporting requirements are stated in appropriate sections as well as in section 7 on reporting.

2.1 Small Signal Calculations from Small Signal Measurements at Zero Field (s,MsE=0)

2.1(a) The small signal dielectric constant, ε^T_{33}, calculated from small signal measurements at zero field is labeled "s,MsE=0" where s signifies a small signal calculation, Ms signifies that the measurement was performed at small signals and E=0 signifies that the measurement is made at a bias field of zero. The dielectric constant calculated in this manner is correctly written ε^T_{33} (s,MsE=0). The value of ε^T_{33} (s,MsE=0) is given by the slope of the polarization versus electric field curve labeled ε^T_{33} (s,MsE=0) in Figure 1.

2.1(b) If the material being tested is not frequency dispersive the value of ε^T_{33} (s,MsE=0) will be the same as the value of ε^T_{33} measured by ASTM Standard D 150-74. If the material is frequency dispersive then the value of

ε^T_{33} (s,MsE=0) will not be the same as the value of ε^T_{33} measured by ASTM Standard D 150-74 unless the two test frequencies are the same.
2.1(c) The small signal piezoelectric coefficient, d_{33}, calculated from small signal measurements at zero field is labeled "s,MsE=0" where s signifies a small signal calculation, Ms signifies that the measurement was performed at small signals and E=0 signifies that the measurement is made at a bias field of zero. The piezoelectric coefficient calculated in this manner is correctly written d_{33} (s,MsE=0). The value of d_{33} (s,MsE=0) is given by the slope of the strain versus electric field curve labeled d_{33} (s,MsE=0) in Figure 3.
2.1(d) If the material being tested is not frequency dispersive the value of d_{33} (s,MsE=0) will be the same as the value of d_{33} measured by ANSI/IEEE Standard 176-1987. If the material is frequency dispersive then the value of d_{33} (s,MsE=0) will not be the same as the value of d_{33} measured by ANSI/IEEE Standard 176-1987 unless the two test frequencies are the same.

2.2 Small Signal Calculations at an Arbitrary Bias Field from Small Signal Measurements (s,MsE=A)
2.2(a) The small signal dielectric constant, ε^T_{33}, calculated from small signal measurements at an arbitrary bias field is labeled "s,MsE=A" where s signifies a small signal calculation, Ms signifies that the measurement was performed at small signals and E=A signifies that the measurement is made at a nonzero bias field. The dielectric constant calculated in this manner is correctly written ε^T_{33} (s,MsE=A). The value of ε^T_{33} (s,MsE=A) is given by the slope of the polarization versus electric field curve labeled ε^T_{33} (s,MsE=A) in Figure 1.
2.2(b) The value of ε^T_{33} (s,MsE=A) will not be the same as the value of ε^T_{33} measured by ASTM Standard D 150-74.
2.2(c) The small signal piezoelectric coefficient, d_{33}, calculated from small signal measurements at an arbitrary bias field is labeled "s,MsE=A" where s signifies a small signal calculation, Ms signifies that the measurement was performed at small signals and E=A signifies that the measurement is made at a nonzero bias field. The piezoelectric coefficient calculated in this manner is correctly written d_{33} (s,MsE=A). The value of d_{33} (s,MsE=A) is given by the slope of the strain versus electric field curve labeled d_{33} (s,MsE=0) in Figure 3.
2.2(d) The value of d_{33} (s,MsE=A) will not be the same as the value of d_{33} measured by ANSI/IEEE Standard 176-1987.

2.3 Small Signal Calculations at an Arbitrary Bias Field from Large Signal Measurements (s,MlE=A)
2.3(a) The small signal dielectric constant, ε^T_{33}, calculated from large signal measurements at an arbitrary bias field is labeled "s,MlE=A" where s signifies a small signal calculation, Ml signifies that the measurement was performed at large signals and E=A signifies that the measurement is made at a nonzero bias field. The dielectric constant calculated in this manner is correctly written ε^T_{33} (s,MlE=A). The value of ε^T_{33} (s,MlE=A) is given by the instantaneous slope of the polarization versus electric field curve labeled ε^T_{33} (s,MlE=A) in Figure 1.
2.3(b) The value of ε^T_{33} (s,MlE=A) will generally not be the same as the value of ε^T_{33} measured by ASTM Standard D 150-74.
2.3(c) The small signal piezoelectric coefficient, d_{33}, calculated from large signal measurements at an arbitrary bias field is labeled "s,MlE=A" where s signifies a small signal calculation, Ml signifies that the measurement was performed at large signals and E=A signifies that the measurement is made at a nonzero bias field. The piezoelectric coefficient calculated in this manner is correctly written d_{33} (s,MlE=A). The value of d_{33} (s,MlE=A) is given by the instantaneous slope of the strain versus electric field curve labeled d_{33} (s,MlE=A) in Figure 3.
2.3(d) The value of d_{33} (s,MlE=A) will generally not be the same as the value of d_{33} measured by ANSI/IEEE Standard 176-1987.

2.4 Large Signal Calculations from Large Signal Measurements (l,Ml)
2.4(a) The large signal dielectric constant, ε^T_{33}, calculated from large signal measurements is labeled "l,Ml" where l signifies a large signal calculation and Ml signifies that the measurement was performed at large signals.

The dielectric constant calculated in this manner is correctly written ε^T_{33} (l,Ml). The value of ε^T_{33} (l,Ml) is given by the slope of the line labeled ε^T_{33} (l,Ml) on the polarization versus electric field curve in Figure 2.
2.4(b) The value of ε^T_{33} (l,Ml) will not be the same as the value of ε^T_{33} measured by ASTM Standard D 150-74.
2.4(c) The large signal piezoelectric coefficient, d_{33}, calculated from large signal measurements is labeled "l,Ml" where l signifies a large signal calculation and Ml signifies that the measurement was performed at large signals. The piezoelectric coefficient calculated in this manner is correctly written d_{33} (l,Ml). The value of d_{33} (l,Ml) is given by the slope of the line labeled d_{33} (l,Ml) on the strain versus electric field curve in Figure 4.
2.4(d) The value of d_{33} (l,Ml) will not be the same as the value of d_{33} measured by ANSI/IEEE Standard 176-1987.

3. SAMPLE PREPARATION

3(a) Poling the sample is necessary to minimize domain reorientation contributions to the field dependent polarization and strain behavior. Poling does not, however, guarantee a stable domain state. It is advisable to check the quality of the poling by measuring the small signal capacitance and the loss tangent before and after poling. In general, the loss tangent should be lower following the poling. High loss tangents can be indicative either of electrically active domain walls or conduction in the material. It would be desirable if the quality of the poling were confirmed with an independent measurement (i.e. pyroelectric coefficient or x-ray diffraction measurements).
3(b) The technique for the measurement of the small signal capacitance and loss tangent is given in ASTM Standard D 150-74 "A-C Loss Characteristics and Dielectric Constant (Permittivity) of Solid Electrical Insulating Materials".

4. MEASUREMENT OF FIELD DEPENDENT POLARIZATION AND STRAIN BEHAVIOR

4(a) This is a protocol for calculation of the dielectric constant and piezoelectric constant rather than a protocol for how to correctly measure the field dependent polarization and strain behavior. Consequently, the measurements themselves are not discussed in great detail, however important or unique aspects for testing electroactive single crystals are noted here.

4.1 Polarization Measurements

4.1(a) Large signal measurements of the polarization as a function of electric field intended for the calculation of either ε^T_{33} (s,MlE=A) or ε^T_{33} (l,Ml) must be performed under unipolar drive conditions. A unipolar drive condition is necessary to ensure that the material is not depoled and that the domain state is not appreciably altered during measurement. Note that in order to produce a unipolar ac signal the internal circuitry of the signal generator applies a d.c. bias to the a.c. field. This is done transparently for the user. Thus, unipolar is not synonymous with zero bias.
4.1(b) If the measurement apparatus is not intended to study the effect of stress in a controlled manner, the set-up used to detect the polarization must not impose much stress on the part to be measured. Clamping by a sample fixture can lower the measured polarization – field response or exaggerate it with stress-induced depoling and subsequent domain reorientation of the sample.
4.1(c) If the domain state is stable and the material is not fully poled, then subsequent measurements of the polarization – field characteristic should be repeatable. Whether a single curve/loop is collected or a composite of numerous curves/loops is gathered to describe the strain-field response depends upon the number of data points needed to accurately calculate the dielectric constant.
4.1(d) If the polarization-field curve characteristics change upon subsequent measurement cycles, then the original domain state is not a stable one. Ideally, the sample should be measured repeatedly until the behavior stabilizes.
4.1(e) If ε^T_{33} (s,MlE=A) or ε^T_{33} (l,Ml) are being calculated and the polarization versus electric field behavior of the materials is hysteretic, then ε^T_{33} measured according to ASTM Standard D 150-74 should also be measured and reported.

4.2 Strain Measurements

4.2(a) Large signal measurements of the strain as a function of electric field intended for the calculation of either d_{33} (s,MlE=A) or d_{33} (l,Ml) must be performed under unipolar drive conditions. A unipolar drive condition is necessary to ensure that the material is not depoled and that the domain state is not appreciably altered during measurement. Note that in order to produce a unipolar ac signal the internal circuitry of the signal generator applies a d.c. bias to the a.c. field. This is done transparently for the user. Thus, unipolar is not synonymous with zero bias.

4.2(b) The measurement frequency should be appropriate for the technique employed to measure strain.

4.2(c) If the measurement apparatus is not intended to study the effect of stress in a controlled manner, the set-up used to detect the strain must not impose much stress on the part to be measured. Clamping by a sample fixture can lower the measured strain – field response or exaggerate it with stress-induced depoling and subsequent domain reorientation of the sample.

4.2(d) If the domain state is stable and the material is fully poled, then subsequent measurements of the strain – field characteristic should be repeatable. Whether a single unipolar curve/loop is collected or a composite of numerous curves/loops is gathered to describe the strain-field response depends upon the number of data points needed to accurately calculate the piezoelectric coefficient.

4.2(e) If the strain – field characteristic changes on subsequent measurement cycles, then the original domain state is not a stable one. Ideally, the sample should be measured repeatedly until the behavior stabilizes.

4.2(f) If d_{33} (s,MlE=A) or d_{33} (l,Ml) are being calculated and the strain versus electric field behavior of the materials is hysteretic, then d_{33} measured according to ASTM Standard D 150-74 should also be measured and reported.

4.2(g) If either d_{33} (s,MlE=A) or d_{33} (l,Ml) are being calculated then d_{33} measured according to ANSI/IEEE Standard 176-19 should also be measured and reported.

5. CALCULATION OF DIELECTRIC CONSTANT, e^T_{33}

5(a) If the domain state is stable and the material is fully poled, the dielectric constant may be calculated from either a single curve/loop or a composite of numerous curves/loops.

5(b) If the original domain state is not a stable one, but the sample is repeatedly measured until the behavior stabilizes, then the dielectric constant may be calculated from either a single, stable curve/loop or a composite of numerous stable curves/loops.

5(c) If the original domain state is not a stable one and the sample cannot be measured until the behavior stabilizes, then only single curves/loops should be employed to calculate the dielectric constant.

5(d) A possible benefit to employing a composite of numerous curves/loops is that the increased number of data points may make curve fitting easier.

5(e) When curve fitting during the calculation of dielectric constant (ε^T_{33}), the portion of the data that is being fit should contain a minimum of 100 points.

5.1 Small Signal Calculations at an Arbitrary Bias Field from Large Signal Measurements: e^T_{33} (s,MlE=A)

5.1(a) The small signal ε^T_{33} (s,MlE=A) value is the instantaneous slope of the polarization-field curve at an arbitrary bias field of interest. Thus, ε^T_{33} (s,MlE=A) = dP_3/dE_3 for large signal measurements centered at an arbitrary bias field.

5.1.1 Anhysteretic Curves

5.1.1(a) The polarization-field data should be curve fit as a function of field. Calculate the instantaneous slope of the fitted polarization-field curve at the bias field level of interest for the value of ε^T_{33} (s,MlE=A) at that bias field.

5.1.2 Hysteretic Curves

5.1.2(a) The polarization-field data can be divided into two sets: 1) a top set which represents polarization behavior under decreasing field, and 2) a bottom set which represents polarization behavior under increasing field. The polarization data in these two sets should be curve fit as a function of field. The two resulting polarization-field curves should be reduced to a single curve that is the average of the two. Calculate the instantaneous slope of the average polarization-field curve at the bias field level of interest for the value of ε^T_{33} (s,MlE=A) at that bias field. Calculate the maximum difference between the increasing and decreasing field curves.

5.2 Large Signal Calculations from Large Signal Measurements: ε^{T}_{33} **(l,Ml)**

5.2(a) In naval sonar applications, electromechanical materials are subject to large electric fields. An "effective" large signal value of the dielectric constant under large electric fields is needed to accurately assess a material's potential performance in these applications. To calculate a large signal dielectric constant, ε^T_{33} (l,Ml) the drive conditions of interest, a dc bias field and a large signal ac drive, need to be established. Knowledge of the drive conditions defines the maximum and minimum electric fields applied to the sample. For example, a sample driven with a dc bias of 0.75 MV/m and an ac drive of 0.50 MV/m p-p is subject to a maximum field of 1.25 MV/m and a minimum field of 0.25 MV/m.

5.2(b) Large signal calculations should be made for the following drive conditions:

0.67 MV/m bias field and 0.34 MV/m rms ac drive

and for any other drive conditions of interest.

5.2.1 Anhysteretic Curves

5.2.1(a) The polarization-field data should be curve fit using a polynomial expansion of order 5 in field. Locate the two points on the fitted curve that correspond to the maximum and minimum fields for the drive conditions of interest. The slope of the straight line between these two points is the effective large signal ε^T_{33} (l,Ml).

5.2.2 Hysteretic Curves

5.2.2(a) The polarization -field data can be divided into two sets: 1) a top set which represents polarization behavior under decreasing field, and 2) a bottom set which represents polarization behavior under increasing field. The polarization data in these two sets should be curve fit as a function of field. The two resulting polarization-field curves should be reduced to a single curve that is the average of the two. Locate the two points on the fitted curve that correspond to the maximum and minimum fields for the drive conditions of interest. The slope of the straight line between these two points is the effective large signal ε^T_{33} (l,Ml).

5.2.2(b) The amount of hysteresis, which represents the equivalent large signal dielectric loss factor (equivalent large signal tan δ) in the loop, should also be calculated using the fitted curves and the following definition:

$$\text{equivalent large signal } \tan\delta = (A_1 + A_2) / [\pi(A_2 + A_3)]$$

where the areas are defined in Fig. 5[1].

6. CALCULATION OF THE PIEZOELECTRIC COEFFICIENT, d_{33}

6(a) If the domain state is stable and the material is fully poled, the piezoelectric coefficient may be calculated from either a single curve/loop or a composite of numerous curves/loops.

6(b) If the original domain state is not a stable one, but the sample is repeatedly measured until the behavior stabilizes, then the piezoelectric coefficient may be calculated from either a single, stable curve/loop or a composite of numerous curves/loops.

6(c) If the original domain state is not a stable one and the sample cannot be measured until the behavior stabilizes, then only single curves/loops should be employed to calculate the piezoelectric coefficient.

6(d) A possible benefit to employing a composite of numerous curves/loops is that the increased number of data points may make curve fitting easier.

6(e) When curve fitting during the calculation of d_{33}, the portion of the data that is being fit should contain a minimum of 100 points.

6.1 Small Signal Calculations at an Arbitrary Bias Field from Large Signal Measurements: d_{33} (s,MlE=A)

6.1(a) The small signal d_{33} (s,MlE=A) value is the instantaneous slope of the strain-field curve at an arbitrary bias field of interest. Thus, d_{33} (s,MlE=A) = dS_3/dE_3 for large signal measurements centered at an arbitrary bias field.

6.1.1 Anhysteretic Curves

6.1.1(a) The strain-field data should be curve fit as a function of field. Calculate the instantaneous slope of the fitted strain-field curve at the bias field level of interest for the value of d_{33} (s,MlE=A) at that bias field.

6.1.2 Hysteretic Curves

6.1.2(a) The strain-field data can be divided into two sets: 1) a top set which represents strain behavior under decreasing field, and 2) a bottom set which represents strain behavior under increasing field. The strain data in these upper set should be curve fit using a polynomial expansion in field. Calculate the instantaneous slope of the average strain-field curve at the bias field level of interest for the value of d_{33} (s,MlE=A) at that bias field. Calculate the maximum difference between the increasing and decreasing field curves.

6.2 Large Signal Calculations from Large Signal Measurements: d_{33} (l,Ml)

6.2(a) In naval sonar applications, electromechanical materials are subject to large electric fields. An "effective" large signal value of the piezoelectric coefficient under large electric fields is needed to accurately assess a material's potential performance in these applications. To calculate a large signal piezoelectric coefficient the drive conditions of interest, a dc bias field and a large signal ac drive, need to be established. Knowledge of the drive conditions defines the maximum and minimum electric fields applied to the sample. For example, a sample driven with a dc bias of 0.75 MV/m and an ac drive of 0.50 MV/m p-p is subject to a maximum field of 1.25 MV/m and a minimum field of 0.25 MV/m.

6.2(b) Large signal calculations should be made for the following drive conditions:

0.67 MV/m bias field and 0.34 MV/m ac drive

and for any other drive conditions of interest.

6.2.1 Anhysteretic Curves

6.2.1(a) The strain-field data should be curve fit using a polynomial expansion in field. Locate the two points on the fitted curve that correspond to the maximum and minimum fields for the drive conditions of interest. The slope of the straight line between these two points is the effective large signal d_{33} (l,Ml).

6.2.2 Hysteretic Curves

6.2.2(a) The strain-field data can be divided into two sets: 1) a top set which represents strain behavior under decreasing field, and 2) a bottom set which represents strain behavior under increasing field. The strain data in these two sets should be curve fit as a function of field. Locate the two points on the fitted curve that correspond to the maximum and minimum fields for the drive conditions of interest. The slope of the straight line between these two points is the effective large signal d_{33} (l,Ml).

7 REPORTING

7.1 General Requirements

7.1(a) Report the following information:

1) Sample preparation, including surface finish
2) Sample geometry
3) Electrode type

4) Date of Poling
5) Date of Measurement
6) Sample clamping conditions
7) Applied stress conditions
8) Unipolar drive conditions: either minimum and maximum fields or d.c. bias and a.c. drive fields
9) Bipolar drive conditions: either minimum and maximum fields or d.c. bias and a.c. drive fields
10) Drive frequency
11) Sample temperature
12) Whether or not the domain state was stable. If the domain state was not stable report whether or not the sample was cycled until the domain state was stable.
13) Whether calculations are based upon a single curve/loop or a composite of numerous curves/loops.
14) For large signal calculations of the dielectric constant and/or the piezoelectric coefficient report the drive conditions used for calculation, even when the standard 0.67 MV/m bias field and 0.34 MV/m ac drive conditions are employed.
15) For s,MlE=A calculations report the bias field at which the measurement is performed.
16) Report whether or not the material was anhysteretic. If the material is hysteretic and small signal measurements are used for the calculations report what field range was employed for the calculation. Also report the calculated maximum difference between the increasing and decreasing field curves.
17) Provide figures of the full curves or loops measured.

7.2 Requirements Specific to Polarization Measurements and Calculation of the Dielectric Constant

7.2(a) If the material is hysteretic report the calculated large signal tan δ.

7.3 Requirements Specific to Strain Measurements and Calculation of the Piezoelectric Coefficient

7.3(a) Report the type of sensor employed for the measurement of the strain

7.4 Other Information If Available

7.4(a) Report the following information:

1) Small signal capacitance and loss tangent measured before and after poling
2) Pyroelectric coefficient
3) Piezoelectric coefficient measured by resonance

8 REFERENCES

1. "Large signal dielectric losses in electrostrictive materials", H.C. Robinson, *Proceedings of the 7th SPIE Symposium on Smart Materials and Structures,* Newport Beach, CA, March '00.

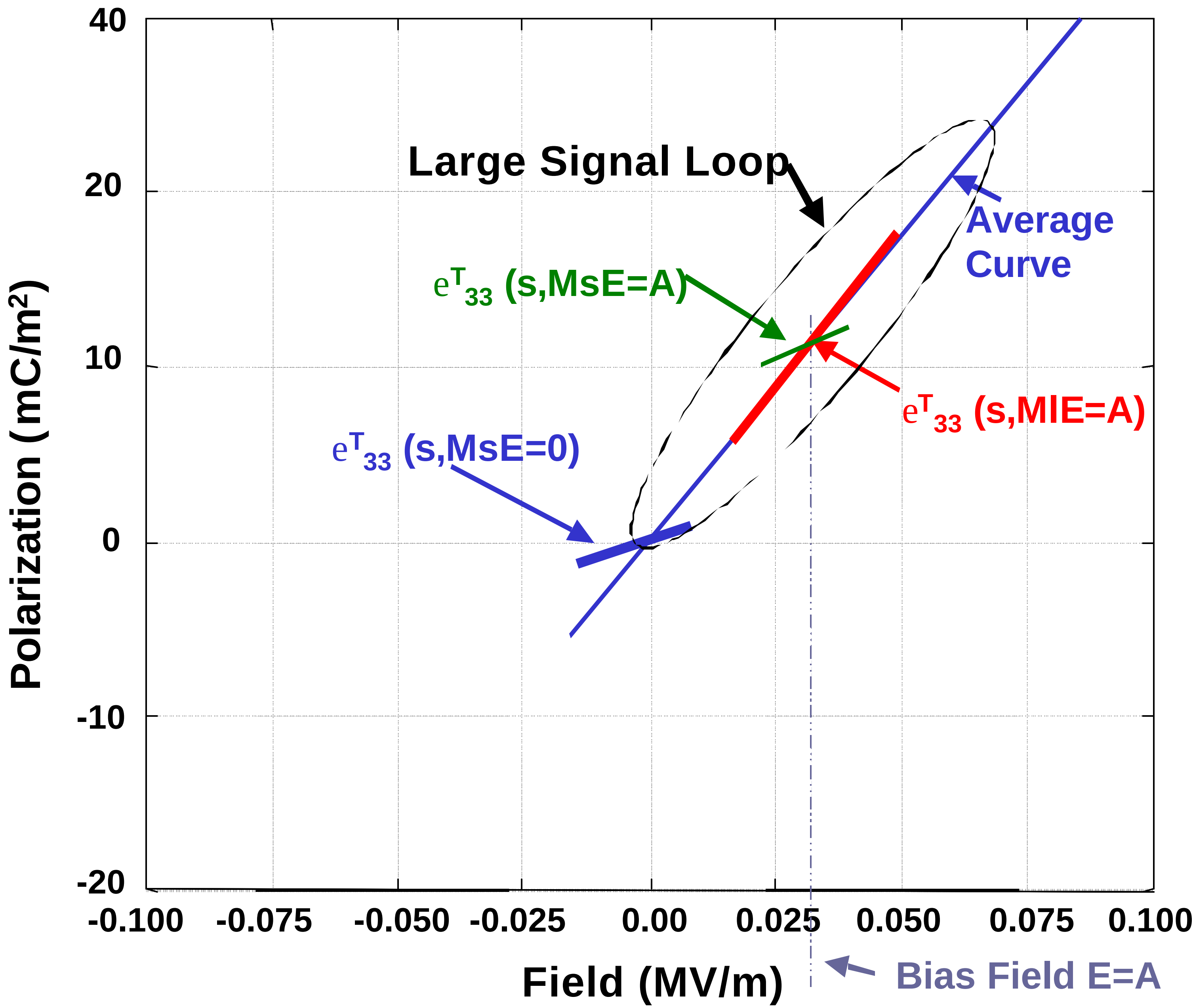

Fig. 1: Definition of e^T_{33} (s,MsE=0), e^T_{33} (s,MsE=A), and e^T_{33} (s,MIE=A)

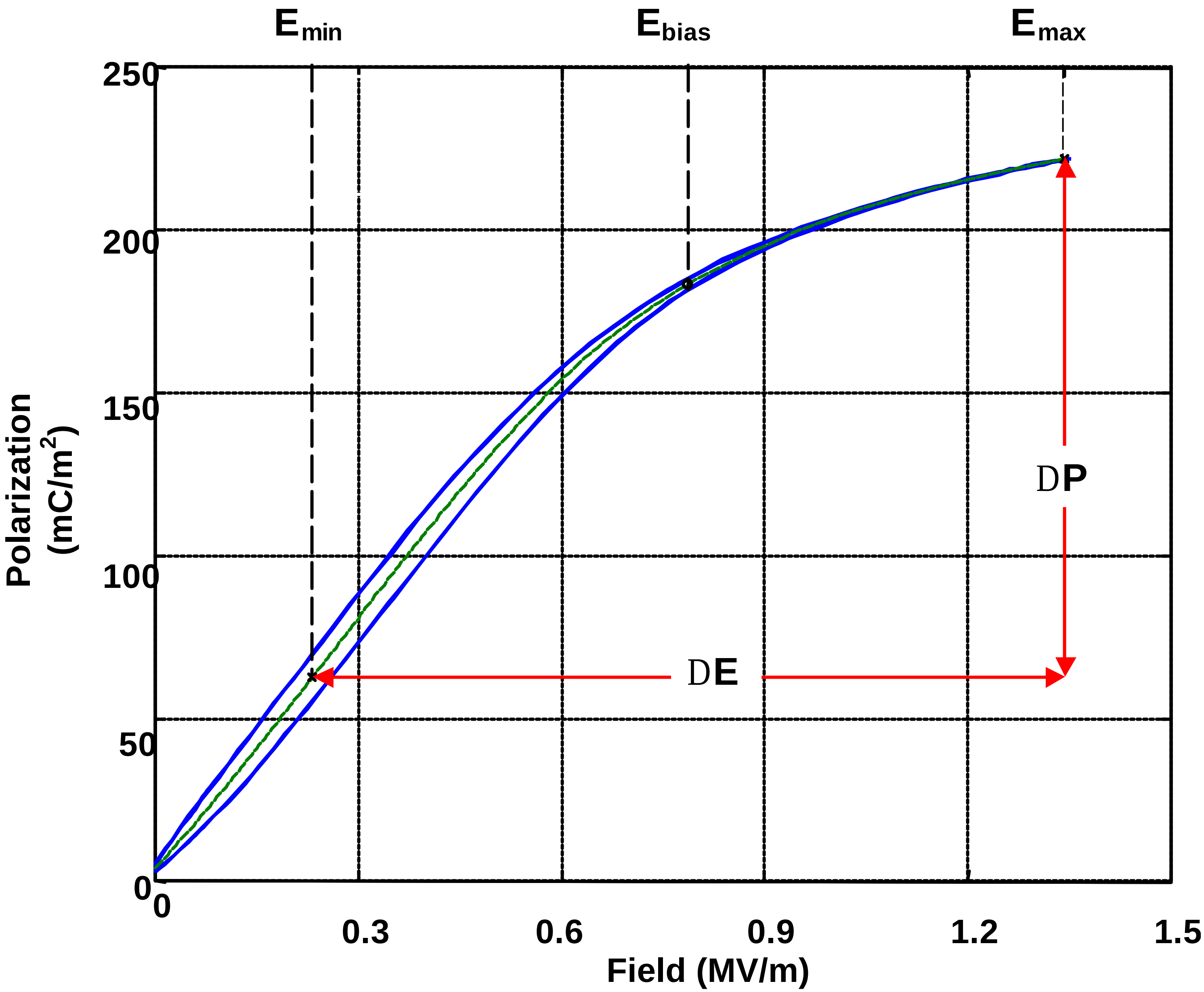

Figure 2. Calculation of effective large signal dielectric constant.
Blue line--measured data; Green line—average curve used to define ε^T_{33} (I,MI).

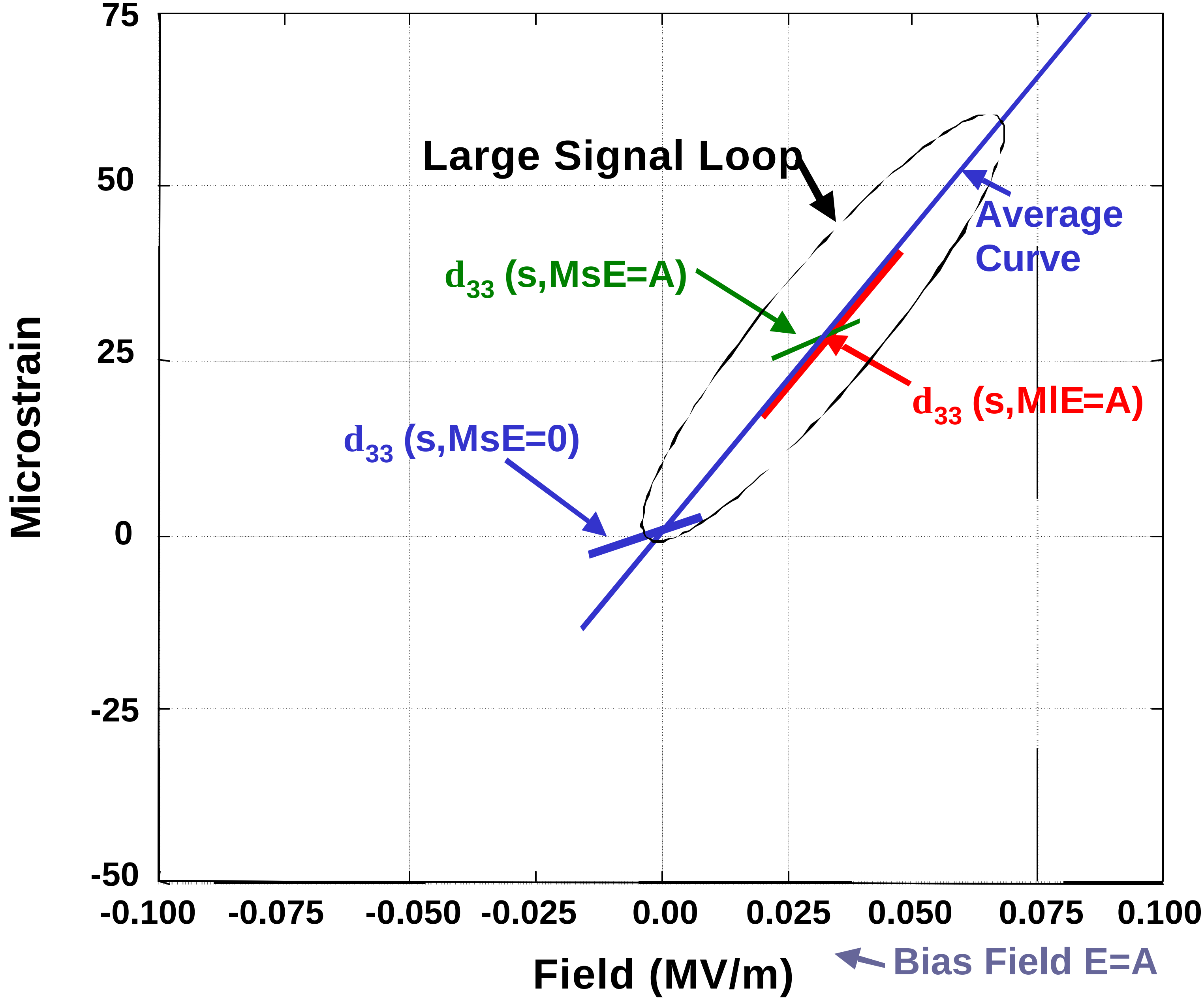

Fig. 3: Definition of d_{33} (s,MsE=0), d_{33} (s,MsE=A), and d_{33} (s,MlE=A)

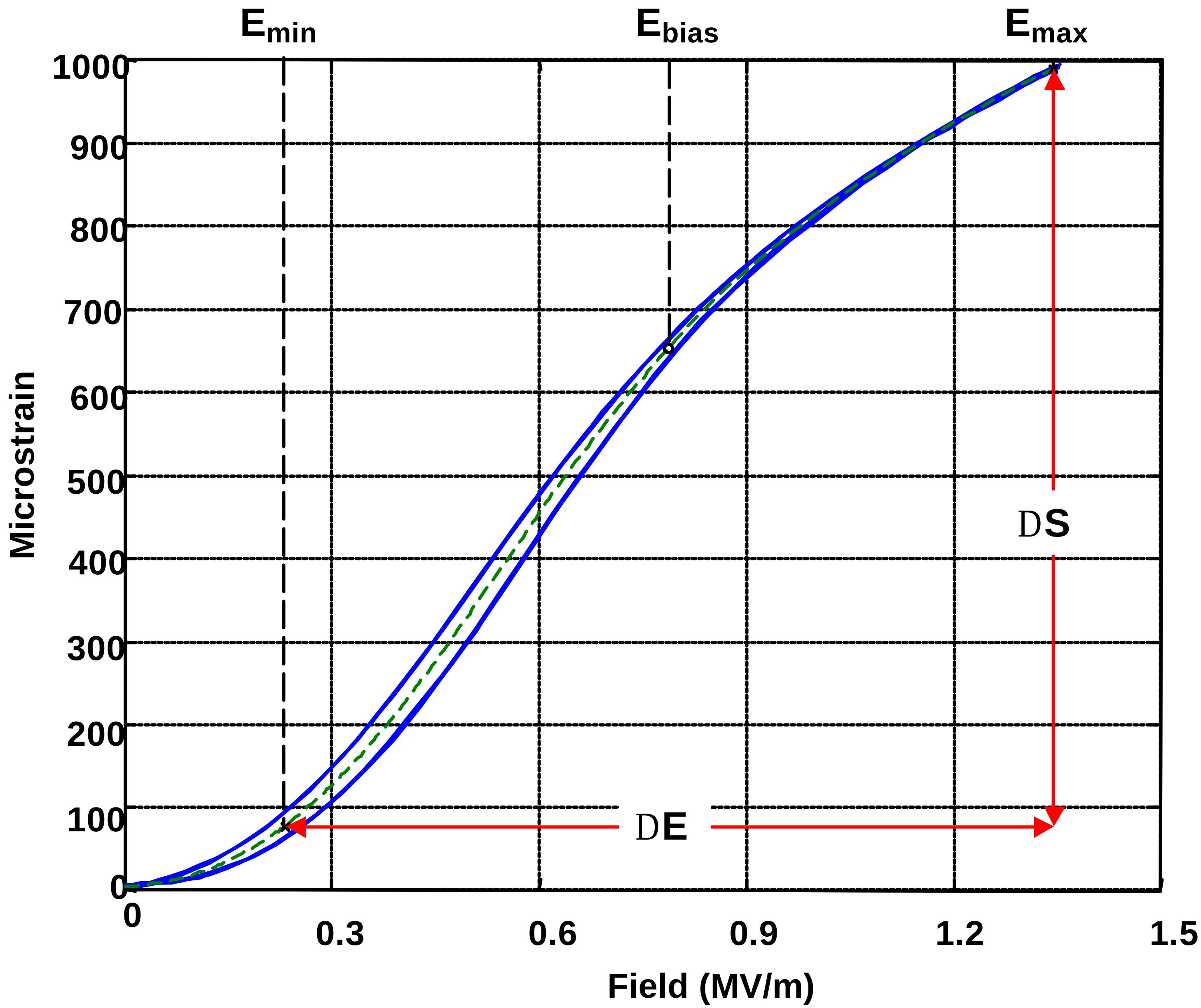

Figure 4. Calculation of effective large signal piezoelectric coefficient. Blue line--measured data; Green line—average curve used to define d_{33} (l,Ml).

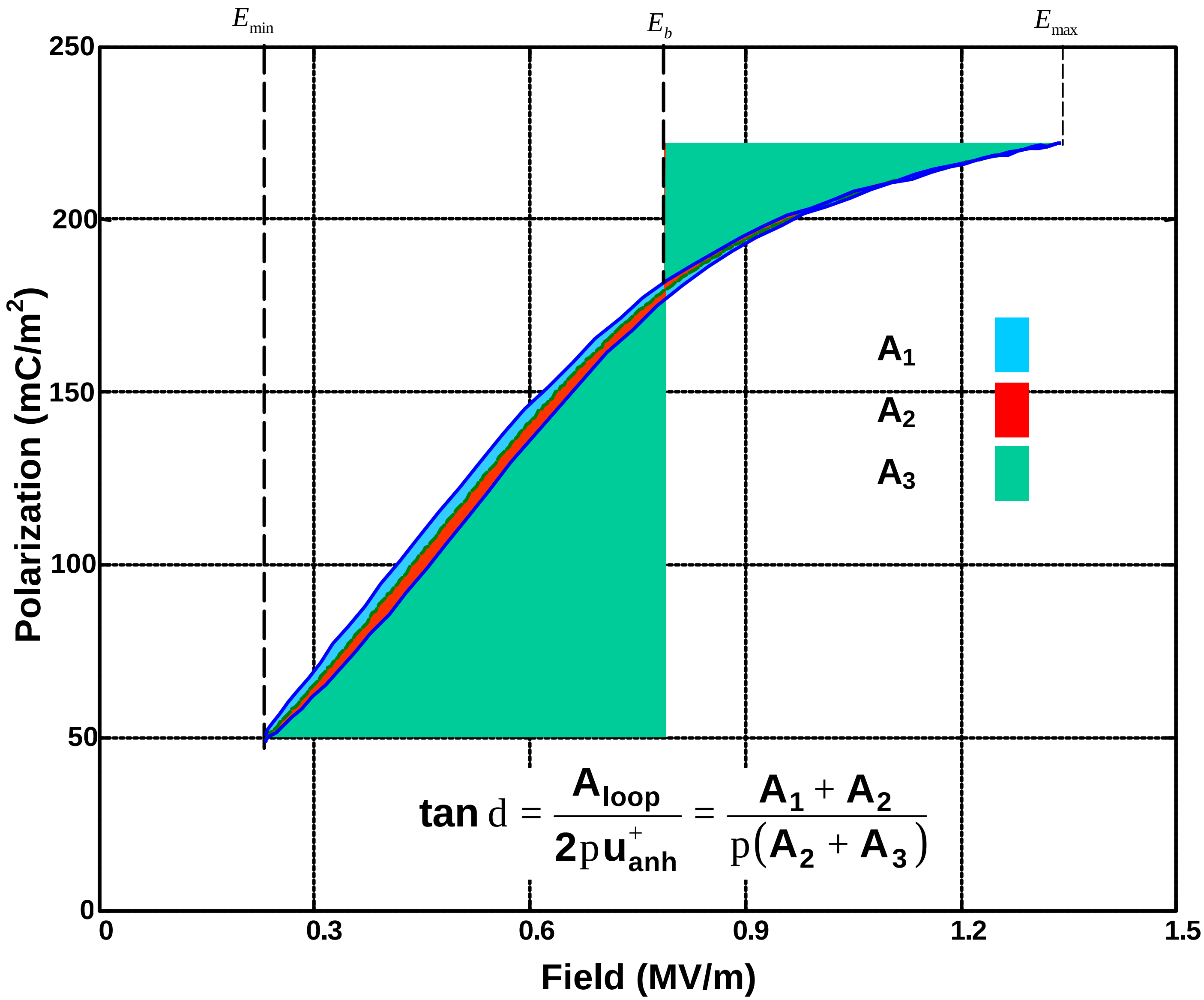

Figure 5. Calculation of equivalent large signal dielectric loss factor. Blue line--measured data, green line--average used to define stored energy.