Content

1. Scope

1.1. This specification covers the physical and electromechanical requirements for relaxor based piezoelectric single crystal materials with inherent multiple domains intended for fabrication into single plates, multilayer plate devices, and composites with other passive materials for use in medical, industrial and military transducers, actuators, and sensors.

1.2. This specification currently covers PMN-PT and PZN-PT single crystal compositions (and can be expanded as new compositions are developed and fully characterized).

1.3. *This standard specification does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish safety requirements and health practices and determine the applicability of regulatory limitations prior to use*.

2. Referenced Documents[1]

2.1. IEEE/ASTM SI10-1997 – Standard for Use of the International System of Units (SI): The Modern Metric System.

2.2. ANSI/IEEE Standard 176 –1987: IEEE Standard On Piezoelectricity.

2.3. ASTM Standard D150-98: Standard Test methods for AC Loss Characteristics And Permittivity (Dielectric Constant) of Solid Electrical Insulation.

2.4. ASTM Standard D2149-97: Standard Test Method for Permittivity (Dielectric Constant) And Dissipation Factor Of Solid Dielectrics At Frequencies To 10 MHz And Temperatures To 500°C.

2.5. ASTM Test Method C559-90: Standard Test Method for Bulk Density by Physical measurements of Manufactured Carbon and Graphite Articles.

2.6. ASTM Test Method D3359-97: Standard Test Methods for Measuring Adhesion by Tape Test.

2.7. ASTM Test Method B 905-00: Standard Test Methods for Assessing the Adhesion of Metallic and Inorganic Coatings by the Mechanized Tape Test.

2.8. ASTM Test Method (XRD measurement)

2.9. J. F. Nye, Physical Properties of Crystals, The Clarendon Press, Oxford 1957.

2.10. Warren P. Mason, "Physical Acoustics, Principles and Methods," Academic Press, New York, 1964.

3. Terminology

3.1. Definitions

3.1.1. buyer – organization issuing the purchase order.

3.1.2. crystal lot – a specified quantity of piezoelectric single crystals with a certain composition from a crystal growth run such that samples taken in accordance with section 11 can represent the entire quantity.

3.1.3. d_{33} – the longitudinal mode piezoelectric coefficient measured using small signal. The subscript indices, as defined by ANSI/IEEE Standard 176-1987, indicate the crystallographic orientation in which the measurement is made. The sets of crystallographic reference axis for the subscript indices determination with respect to the poling direction are presented in section 5.5. The measurement method is defined in ANSI/IEEE Standard 176-1987.

3.1.4. k_{33} – the rod extensional coupling factor with longitudinal excitation of an end electroded bar

[1] Available at www.astm.org

(see Figure 1(a)) measured using small signal. The aspect ratio of width to height should be determined such that the bar displays a distinct rod extensional mode resonance. The sets of crystallographic reference axis for the subscript indices determination with respect to the poling direction are presented in section 5.5. The measurement method is defined in the IEEE Standard of Piezoelectricity (ANSI/IEEE Standard 176-1987).

3.1.5. k_{33}' – the sliver extensional coupling factor of an end electroded sliver (see Figure 1(b)). The aspect ratio of height to width and the crystallographic orientation should be determined such that the bar displays a height mode resonance. The sets of crystallographic reference axis for the subscript indices determination with respect to the poling direction are presented in section 5.5. The measurement method for k_{33} in 3.1.4 can be applied (see Eq. 148 of ANSI/IEEE Standard 176-1987).

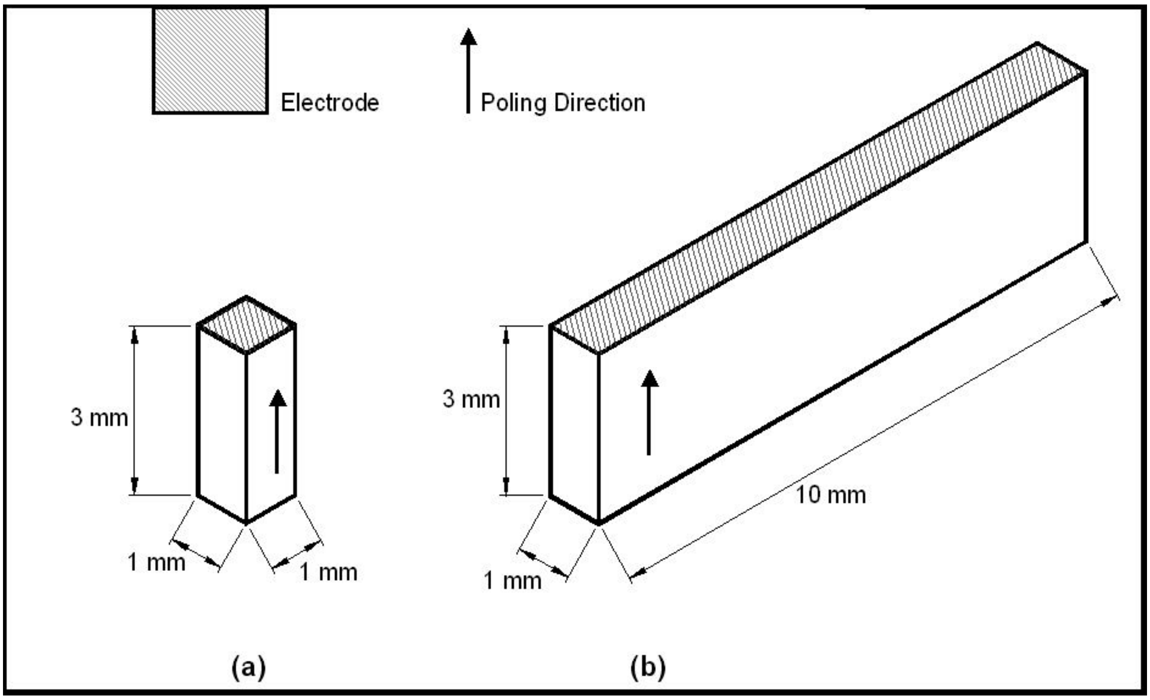


Figure 1: (a) end electroded bar for k_{33} measurement and (b) sliver electroded plate for k_{33}' measurement

3.1.6. K_3^T – the free relative dielectric permittivity of a poled crystal measured along the poling direction. K is the relative permittivity (defined in ASTM Standard D150-98 as K′). The superscript index T is defined in ANSI/IEEE Standard 176-1987 and indicates that the measurement is under constant stress conditions (see ANSI/IEEE Standard 176-1987 section 6.2); therefore, K^T is the free relative dielectric permittivity. The sets of crystallographic reference axis for the subscript indices determination with respect to the poling direction are presented in section 5.5. K_3^T is measured at a temperature between 20°C to 25°C using a small ac signal of less than 5 V_{RMS} at 1 kHz under no electrical and mechanical bias. The value is measured according to ASTM Standard D150-98.

3.1.7. PZN-PT – lead zinc niobate in solid solution with lead titanate. It is referred to as lead zinc niobate - lead titanate. Its chemical composition is $(1-x)Pb(Zn_{1/3}Nb_{2/3})O_3 - xPbTiO_3$, where x ranges from 0 to 1.

3.1.8. PMN-PT – lead magnesium niobate in solid solution with lead titanate. It is referred to as lead magnesium niobate - lead titanate. Its chemical composition is $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3 - xPbTiO_3$, where x ranges from 0 to 1.

3.1.9. s_{33}^D – the elastic compliance at constant electric displacement (equivalent to the open circuit elastic compliance) measured using small signal. The sets of crystallographic reference axis for the subscript indices determination with respect to the poling direction are presented in section 5.3. The measurement method is defined in ANSI/IEEE Standard 176-1987.

3.1.10. seller – piezoelectric single crystal supplier.

3.1.11. T_{max} – the temperature at which the maximum free relative dielectric permittivity occurs when measured during cooling from temperatures above 200°C at 1 kHz under no electrical and mechanical bias. The variation in free relative dielectric permittivity with sample temperatures is measured according to ASTM Standard D2149-97.

3.1.12. T_{RT} – the temperature of the first peak or discontinuous anomaly in free relative dielectric permittivity versus temperature curve, measured during heating of unpoled crystals at 1 kHz under no electrical and mechanical bias. The variation in free relative dielectric permittivity with sample temperatures is measured according to ASTM Standard D2149-97.

3.1.13. T_{DP} – the temperature of the first peak, or discontinuous anomaly in free relative dielectric permittivity versus temperature curve, measured during heating of a poled crystal at 1 kHz under no electrical or mechanical bias. The variation in free relative dielectric permittivity with sample temperatures is measured according to ASTM Standard D2149-97.

3.1.14. tan δ – the dielectric loss tangent (dissipation factor) of a poled crystal measured along the poling direction at between 20°C to 25°C using a small AC signal of less than 5 V_{RMS} at 1 kHz under no electrical and mechanical bias. The value is measured according to ASTM Standard D150-98.

3.2. Units – All physical constants appearing in this standard are written in the International System of Units (SI units), according to IEEE/ASTM Standard SI 10-1997.

4. Composition

4.1. This standard covers both PMN-PT and PZN-PT single crystals. Compositions with the most utility have a PT content that is either at or below the morphotropic phase boundary (MPB). For PMN-PT, the MPB composition has 32-35% PT. For PZN-PT, the MPB composition has 9-10% PT.

5. Orientation

5.1. The crystallographic orientation with respect to the poling direction and the working electrode placement determines the properties of the crystal sample.

5.2. Crystal Orientation

5.2.1. The crystal orientation of the sample is designated by associating a crystallographic direction (see Figure 2) with at least one pair of parallel faces of the sample. The piezoelectric crystals are oriented using single crystal X-ray diffraction techniques. The crystal manufacturer shall determine the method of orientation in accordance with the buyer's requirements.

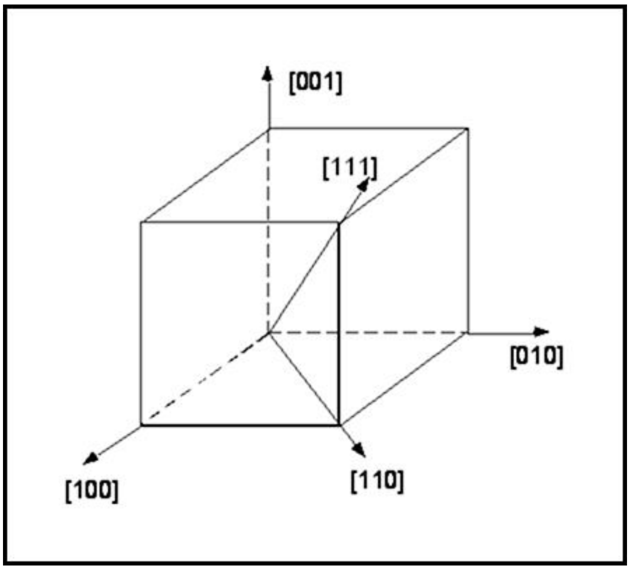


Figure 2: Crystallographic Indices on the basis of Perovskite Unit Cell

5.2.2. Determine the tolerance on the crystal orientations in accordance with the classification and requirements in section 7, or the application specified by the buyer**.**

5.3. Poling Direction

5.3.1. The poling direction is designated by indicating the faces to be electroded for poling and the crystallographic direction perpendicular to the faces. Issues associated with poling are discussed in the appendix.

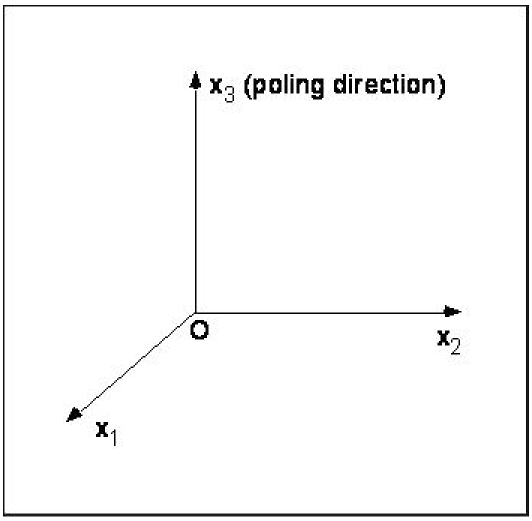
5.3.2. The poling direction shall be marked on each single crystal sample according to the convention in which a dot (•) represents the upward direction of the poling vector and an x (**x**) represents the downward direction of the poling vector. Each sample shall be marked with either a dot or an x or both.

5.4. Working Electrode Placement

5.4.1. In some cases, the poling electrodes can be used as the working electrodes. If the working electrodes are different from the poling electrodes, the poling electrodes will be removed. Placement of the working electrodes is designated by indicating the faces to be electroded and the crystallographic direction perpendicular to the faces.

5.5. Axis of Reference

5.5.1. The axes of reference shall be chosen according to Figure 3. The electromechanical properties calculated by transformation from one set of axes to another using simple transformation equations according to the reference (J. F. Nye, Physical Properties of Crystals, Oxford 1957) may be different from real electromechanical properties, due to the domain configuration changes associated with the poling.



Poling Direction	x_1	x_2	x_3
[001]	[100]	[010]	[001]
[111]	$[1\bar{1}0]$	$[11\bar{2}]$	[111]
[011]	$[0\bar{1}1]$	[100]	[011]

Figure 3: Axes of Reference

Poling Direction	x_1	x_2	x_3
[001]	d_{31}	d_{31}	d_{33}
[111]	d_{31}	d_{31}	d_{33}
[011]	d_{31}	d_{32}	d_{33}

(alternative option) Figure 3: Axes of Reference

5.6. Examples

5.6.1. Crystals poled in the [001] with the working electrode normal to the [001] (Figure 4a)) offer large longitudinal mode piezoelectric coefficients.

5.6.2. Large transverse piezoelectric coefficients are obtained from crystals poled in the [011] with working electrodes in the [011] direction. The transverse direction with the largest piezoelectric coefficient in the crystal is [100] (Figure 4b)).

5.6.3. Crystals poled along the [111] with working electrodes perpendicular to the [110] provide large thickness shear excitation (Figure 4(c)), but these crystals are susceptible to depoling due to domain instability.

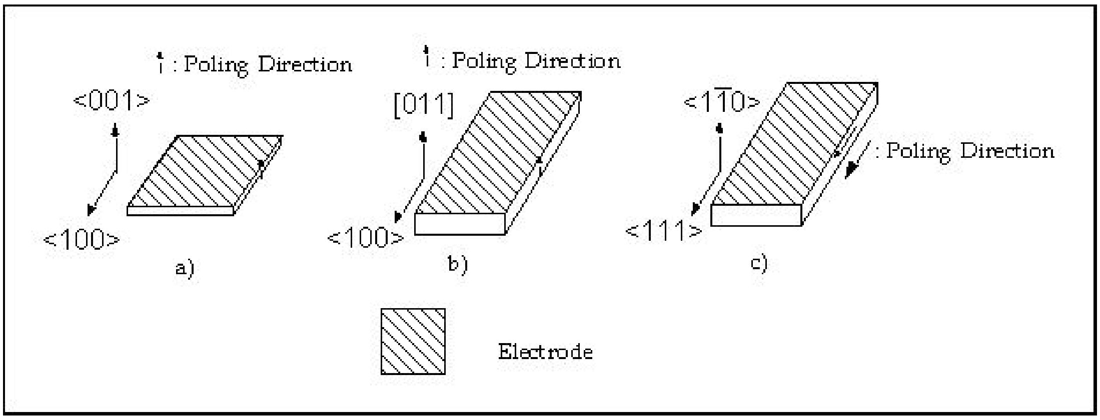


Figure 4: Crystallographic Orientation Examples

5.7. Density - Porosity

5.7.1. $PbTiO_3$ content variation and additive incorporation will change the theoretical density of the crystal. The density measurement method shall be in accordance with ASTM Test Method C559-90.

5.7.2. The porosity measurement method shall be agreed upon between the buyer and the seller. The maximum acceptable percent porosity shall be specified by the buyer.

5.7.3. The number of samples to be tested to meet acceptance criteria shall be agreed upon between the buyer and the seller.

5.8. Phase Purity

5.8.1. The crushed sample of the crystal shall be examined using powder X-ray diffraction. The diffraction pattern must show the pattern of the perovskite phase and no peak originated from other phases shall be observed.

5.8.2. The sampling to determine phase purity shall be mutually agreed upon between the buyer and the seller.

5.8.3. No visible defect such as inclusions shall be observable by transmission optical microscopy with x100 magnification.

6. Classification and Requirements

6.1. Type I – PZN-PT

	Type IA	*Type IB*	*Type IC*
Proposed Composition	PZN-xPT	PZN-xPT	PZN-xPT
	X~0.045	X~0.065	X~0.08
Orientation of Poling	<001>	<001>	<001>
Density (g/cm^3)	≥ 8.25	≥ 8.25	≥ 8.25
K_3^T	4000 – 5500	6700-8000	3000 – 4000
tan δ	≤ 0.015	≤ 0.015	≤ 0.015
T_{RT} (°C, 1kHz)	105 ± 3	100 ± 3	65 ± 3
T_{DP} (°C, 1kHz)	≥ 102	≥ 97	≥ 62
k_{33}	≥ 0.89	≥ 0.92 - 0.94	≥ 0.91
d_{33} (pC/N)	1380 – 2100	2500-3000	1340 - 1900
s_{33}^D (10^{-12} m^2/N)	14-18	14-18	14-18

Orientation of Poling	<110>	<110>	<110>
d_{33} (pC/N)	Value here	Value here	Value here

*All listed properties are measured from poled crystals, except T_{RT}

6.2. Type I – PMN-PT

Type	*Type IIA*	*Type IIB*	*Type IIC*
Proposed Composition	PMN-xPT	PMN-xPT	PMN-xPT
	X ~ 0.28	X ~ 0.30	X ~ 0.32
Orientation of Poling	<001>	<001>	<001>
Density (g/cm^3)	≥ 8.0	≥ 8.0	≥ 8.0
K_3^T	4500 -5500	5500 - 6500	6500 – 7500
tanδ	≤ 0.015	≤ 0.015	≤ 0.015
T_{RT} (°C, 1kHz)	95 ± 3	85 ± 3	75 ± 3
T_{DP} (°C, 1kHz)	≥ 92	≥ 82	≥ 72
k_{33}	≥ 0.88	≥ 0.90	≥ 0.92
d_{33} (pC/N)	1100 - 1700	1450 – 2100	1800 – 2700
s_{33}^D (10^{-12} m^2/N)	10-14	10-14	10-14

Orientation of Poling	<110>	<110>	<110>
d_{33} (pC/N)	Value here	Value here	Value here

*All listed properties are measured from poled crystals, except T_{RT}

6.2. For measurement of properties listed in these tables, poling electrodes shall be working electrodes and low temperature sputtered or vacuum evaporated Au or metal/Au with thickness less than 2000 Å shall be used.

6.3. d_{33} may be measured using a Berlincourt meter. Although this is a non-destructive measurement, the tested samples may experience partial depoling due to the compressive stress applied during the measurement. Thus, it is recommended that the test be performed on only selected samples. If a tested sample is to be sold, re-poling prior to packaging is recommended according to the section 9.

6.4. The provision of k_{33}' sliver extensional coupling factor may be required by the buyer according to the application.

6.5. Sampling plans for the measurements, as the method of compliance with this specification shall be determined according to the section 9.

7. Surface condition and Electrodes

7.1. Slice and polish the crystals with respect to the desired crystallographic orientation. Achieve flat and parallel surfaces on which electrodes are formed. Surface conditions and electrode types shall be mutually agreed upon between the buyer and the seller.

7.2. Unless otherwise specified by the buyer, standard tape testing shall be used to test electrode adhesion according to ASTM Standard Test Methods D3359-97 or ASTM Standard Test Methods B905-00.

8. Poling

8.1. Crystal manufacturers shall determine the poling method to minimize the domain reorientation after poling. Both incomplete poling and over-poling shall be avoided. Poling methods are described in the following.

8.1.1. **Room temperature poling** - Crystals of Types IA and IIA are rhombohedral and the chemical compositions are reasonably away from Morphotropic Phase Boundary (MPB). The poling can be completed by applying 10 kV/cm for less then 1 minute at room temperature.

8.1.2. **Field cooling** – Lowering the temperature of the crystal from above Tmax under bias as high as 10 kV/cm. If single domain crystals must be obtained, incomplete poling due to domain instability is of concern and this poling method can enhance the completeness of poling. However, as crystals classified in section 6 are generally poled along off-polar axis, the field cooling technique may result in over-poled crystals.

8.1.3. **Low temperature poling** - For <001> oriented PZN-PT or PMN-PT single crystals located close to MPB (i.e., type IB and type IIB in section 6), over-poling and subsequent phase variation within the crystal can become important sources of property variation. This method utilizes the curved morphotropic phase boundary. The temperature decrease results in a crystal composition further away from MPB and an increase in E-field required for the phase transition. As a consequence, poling at low temperatures reduces or eliminates the possibility of over-poling. The required magnitude of the electric field and the temperature varies according to the composition. – Over-poling described the application of a too large electric field which causes permanent damage to the crystal due to microcracks and density variation; furthermore local overpoling induces phase transition in the crystal.

9. Sampling for inspection

9.1. Sampling for inspection varies according to the application. Therefore, sampling plans for inspection as the method of compliance with this specification shall be described in the purchase order documents and approved by the buyer.

9.2. The seller shall inspect the crystals in compliance with the plans approved by the buyer and shall provide the inspection results to the buyer. The seller shall certify that each crystal lot is in compliance with the provisions of this specification.

10. Visual Appearance

10.1. The acceptance criteria for visual imperfections in the crystals, including surface chipping, cracks, and inclusions, shall be agreed upon between the buyer and the seller. The inspection method must be agreed upon between the buyer and the seller.

11. Test Method

11.1. Low field measurements according to ANSI/IEEE Standard 176-1987 – After poling, crystal samples shall be stored for at least 24 hours at temperatures between 15^{o}C to 25^{o}C prior to all measurements, unless other conditions are specified.

11.2. T_{max} measurement for the uniformity test.

11.2.1. Increase temperature of oven where the crystals and appropriate bridges are located to 200^{o}C at the rate of less than 10^{o}C/min and maintain the temperature at 200^{o}C for at least 10 minutes.

11.2.2. Decrease the temperature at the rate of less than 2^{o}C/min and record the capacitance at 1 kHz more than 10 points per minute.

11.2.3. T_{max} is the temperature where the largest value of capacitance is recorded.

APPENDIX

A. Crystal Uniformity within the plate or wafer

a) Define sampling method according to the section 9.1.

b) Unless otherwise agreed upon between the buyer and the seller, T_{max} shall be the measure of crystal uniformity.

c) Make five circular electrodes on the surface of the crystal plate or wafer as shown in Figure 5. The diameter of the electrodes shall be approximately 3 mm and the distance of the electrode edge from the crystal edge shall be less than 1 mm.

d) Measure T_{max} according to section 12.2 of this specification.

e) (current option) T_{max} variation for the five electroded areas in the wafer shall be less than $\pm$ 2^o for type I crystals in section 7 and less than $\pm$ 3^o for type II crystals in section 7.

f) (alternative option) The clamped dielectric constant for the five electroded areas in the wafer shall be less than XX (value) for type I crystals and less than XX (value) for type II crystals.

g) (alternative option) The measurement of the capacitance for the five electroded areas in the crystal wafers shall be less than XX (value) for type I crystals and less than XX (value) for type II crystals.

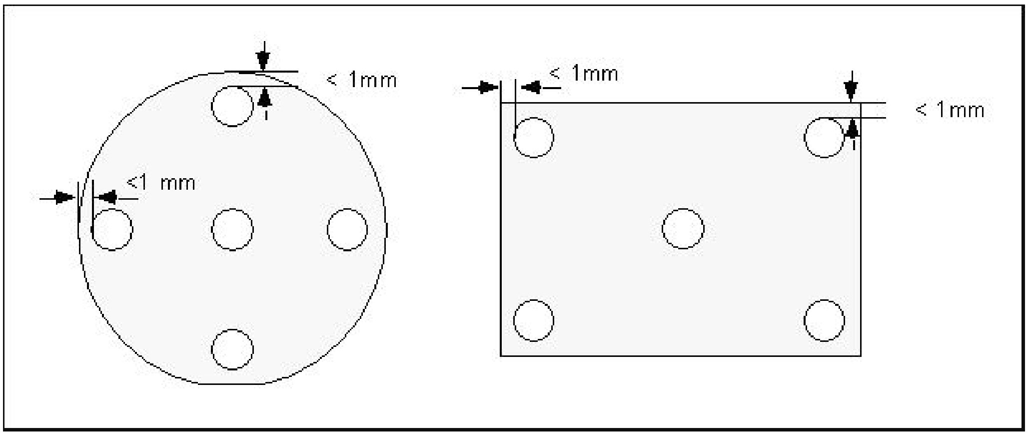


Figure 5: Electrode patterns for uniformity measurement

B. Purchase Information Requirements

a) Composition

b) Size and tolerance

c) Crystal Orientation

d) Poling Direction

e) Working electrode placement

f) Poling condition

g) Polarity – Polarity shall be marked with a black dot on the positive surface

h) Surface Condition

i) Electrode

j) Quantity

k) Unit Price and Total Price

C. Packaging

a) Package the material in standard commercial containers designed to protect the crystal from damage, and constructed to ensure safe transportation at the lowest rate to the point of delivery, unless otherwise specified in the purchase order document.

b) Poled crystals must be maintained in short circuit conditions during shipping; wrap crystals in metal foil before transportation.