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**SOME OF THE THINGS THAT ARE KNOWN AND SOME THAT SHOULD BE KNOWN
ABOUT PIEZOELECTRIC CERAMIC***

Sandia Corporation's interest in this field is somewhat different than that of the average company represented at this meeting. In this field of piezoelectric ceramics, there are certain materials or processing "trade secrets" held by the producers. In addition, due to the state of the knowledge of many variables affecting performance of the ceramics under their application conditions, we recognize the necessity of currently defining Sandia procurement by specifications that lack much of what we call "complete manufacturing information". It is our primary aim to assure production availability of high quality, reliable ceramics for Sandia applications in a competitive supplier atmosphere by means of such performance specifications. If such high quality and reliability of uniform product can be obtained without our imposing complete specifications on materials and process controls, our requirements can be met. Sandia is chiefly interested in the products that are being turned out. How uniform are these products? What are their physical characteristics? Are these characteristics measured in a manner making them applicable to certain applications? And, if there are techniques and procedures for altering and improving these physical constants when they fail to meet specifications. Sandia Corporation does not wish to urge any of the fabricators of these materials to share their "know how" with their competitors. Sandia Corporation does, however, intend to continue to be as helpful in this field as possible by giving freely, to all fabricators, the benefit from any research or development work originated and done at this installation, such as measuring facilities, techniques, etc.

During the past four or five years at Sandia certain things have become quite well known about these compositions. For instance in the earlier days these piezoelectric compositions were used primarily in transducers where mechanical stresses were slight, or if they were electrically driven the driving voltage was quite low. Whereas, now it is common practice to stress these elements up to 25,000 or 30,000 psi to generate voltage or energy pulses. These high stresses when applied quickly (in micro-seconds) introduce problems in mechanical uniformity and crushing strength, whereas when stresses are applied slowly (in a few seconds) they create resistivity problems. Furthermore, operation over wide temperature ranges is being requested in many of these applications. Barium titanate ceramic has been fairly satisfactory in efficiency and uniformity over its useful temperature range, but it can only be used up to about 90°C and even at this low top temperature one must tolerate considerable increases in conductivity in the upper range. These limitations have been the cause of rather extensive research and development work to produce a piezoelectric ceramic showing equal or better efficiency while demonstrating more uniform physical characteristics over a much wider temperature range (up to 425°C).

Lead zirconate-lead titanate (PZT) and lead metaniobate compositions are a result of these demands. The early work on lead zirconate-lead titanate compositions was done at The Bureau of Standards and is being

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continued to some considerable degree at other research installations under various names. Most of the development work on lead metaniobate has been done at General Electric. Both of these compositions show much higher Curie points, 380° and 575°C respectively, permitting operation without much deterioration close to these temperature points. Both have lower dielectric constants, 600 to 1000 for PZT, depending on composition, and approximately 280 for the lead metaniobate. Both are known to show rather high electrical conductivity in the upper temperature range. To date this conductivity at the higher temperature has been somewhat of a handicap. It tends to limit the degree of poling or activating by limiting the potential that may be applied at elevated temperature, where the poling is usually done. This conductivity is also detrimental to most of the higher temperature applications.

PZT when working into a high impedance, shows an efficiency of about $2\frac{1}{2}$ times that of barium titanate as either a voltage or energy generator when stressed to 200 to 30,000 psi. Lead metaniobate is about equal in efficiency to PZT as a voltage generator, under these conditions and in this stress range, but drops to about $\frac{1}{2}$ the efficiency of PZT as an energy generator. (See attached table.)

Some other compositions have come forth to answer the current demands, but they are at this time believed to be secondary to the two just described.

When comparing efficiencies of these compositions, conditions were specified because it has been shown that PZT when highly stressed quasi-statically, while working into a large capacity, (500 x the element cap.) will effectively produce about 5 times as much charge and resultant voltage as the d_{33} measured at 200 psi (with a shunt cap. of from 50 to 150 times the element cap.) indicates it should. If this charge and resultant voltage are measured on release of stress they are somewhat lower, about $3\frac{1}{2}$ times what they should be. This phenomenon has not been fully explained, but apparently it is not due to depoling since the original d_{33} value has been checked after a number of such stressing operations. More work must be done to establish just which physical constants are changed sufficiently by this relation between mechanical and electrical stress to bring about this abnormal charge.

During Sandia's period of interest, close observations have been made to check physical constants demonstrated by the 4W% lead titanate barium titanate specimens received from the suppliers. This composition has been more or less standard for Sandia's applications. The dielectric constant has increased from about 900 to 1600 or 1700. Electromechanical coupling has varied somewhat; for the most part, some slight improvement has been observed. The piezoelectric coefficient (d_{33} is our prime interest) has also shown considerable increase over this period. Consequently voltage and energy for a given stress has increased somewhat. This is, in general, quite pleasing but it adds to the difficulties for our suppliers to keep their products within specifications covering these elements. To date, our specifications, wherever possible, have been relaxed to ease this situation for the suppliers.

It has been shown that purity content and uniformity of crystal structure of raw materials, mixing and forming techniques, fabricating procedures, electrodes and electrode application, poling procedures, etc. all play an important part in the uniformity and stability of the physical constants of interest.

Following this outline of some of the things that are known, I shall raise some questions as to what has been done or is being done about some of the things that should be known in this piezoelectric field.

NOTE - Space has been left between each question for adding notes.

I. A. Are there some generally accepted procedures and techniques for evaluating raw materials used in the fabrication of piezoelectric ceramic as to uniformity of crystal structure, purity content, particle size, etc. to insure physical constants within definite limits, for specimens when fabricated by precise procedures from mixing to poling?

B. If by such an evaluating procedure the above factors for the raw materials are found to be on one end or the other of the allowable spread, are there any prescribed changes, or additional operations that may be introduced in the fabricating procedures which will correct the effects expected from such faulty raw materials to a degree whereby specimens may be produced showing physical constants within prescribed limits?

C. When test specimens are produced which demonstrate variations in physical constants of considerable magnitude are there any recognized techniques for reconciling these changes with the physical bodies of the specimens?

II. A. Are any of the suppliers of these piezoelectric ceramics equipped with the "know-how" and facilities for evaluating test specimens in a manner to supply data that will apply accurately to highly stressed elements, working under the different circuit conditions that have been outlined?

B. Are there any definite specifications and facilities for evaluating physical constants, as a function of temperature, mechanical stress, electrical stress, circuit conditions (shunt capacity primarily) and various combinations of these factors?

C. Have efforts to reconcile some of the irregularities that have been outlined relating to generated charge, resultant voltage, energy developed, etc., been attributed to changes brought about in any one physical constant or any combination of several?

III. Has any effort been made to design automatic or semiautomatic instrumentation for measuring charge, resultant voltage and energy output from piezoelectric ceramic upon impact and quasi-static stress over some considerable range as a function of temperature (-75° to +425°C)? Interest would be high in such a unit capable of testing 500 to 1000 a day, which would automatically record the data.

IV. Have any reliable facilities been set up for accurately measuring conductivity of these materials, at various voltage gradients, as a function of temperature under stressed and unstressed conditions?

V. What investigations are being made to evaluate physical constants for various percentage mixes of lead zirconate lead titanate (PZT compositions) as a function of mechanical and electrical stress over its usable temperature range?

VI. Are accurate records kept on aging characteristics of PZT under mechanical and electrical stress as a function of temperature?

VII. What data are available on irradiation effects on PZT or piezoelectric ceramic in general, such as exposure to gamma rays and fast neutrons?

VIII. What investigations are under way to evaluate electrode material and application to determine uniformity and reliability at various atmospheric conditions and over the whole usable temperature range?

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Attachment - Table I

TABLE 1

Efficiencies of 53/47 mol % PZT and Lead Metaniobate Compared to 4W % Lead Titanate Barium Titanate

When stressed in compression while working into a high impedance it can be shown that the efficiencies of these materials as a voltage generator is proportional to piezoelectric constant (d_{33}) / dielectric constant (k) and as an energy generator is proportional to (piezoelectric constant)² / dielectric constant.

PZT vs . barium titanate ($BaTiO_3$)

As a Voltage generator

$$PZT = \frac{d_{33}}{K} = \frac{2}{650} = .00307$$

$$BaTiO_3 = \frac{1.7}{1300} = .0013$$

$$Ratio = \frac{.00307}{.0013} = 2.36$$

As an Energy generator

$$PZT = \frac{d_{33}^2}{K} = \frac{4}{650} = .0061$$

$$BaTiO_3 = \frac{(1.7)^2}{1300} = \frac{2.88}{1300} = .0022$$

$$Ratio = \frac{.0061}{.0022} = 2.77$$

Lead metaniobate vs. barium titanate

As a VOLTAGE generator

$$\text{Lead metaniobate} = \frac{d_{33}}{K} = \frac{2.9}{280} = .0032$$

$$BaTiO_3 = \frac{1.7}{1300} = .0013$$

$$Ratio = \frac{.0032}{.0013} = 2.46$$

As an ENERGY generator

$$\text{Lead Metaniobate} = \frac{d_{33}^2}{K} = \frac{.81}{280} = .00286$$

$$\text{BaTiO}_3 = \frac{(1.7)^2}{1300} = \frac{2.88}{1300} = .0022$$

$$\text{Ratio} = \frac{.0029}{.0022} = 1.30$$