CANADA

ELECTROMECHANICAL PROPERTIES OF THREE EXPERIMENTAL LEAD ZIRCONATE-LEAD TITANATE CERAMIC COMPOSITIONS

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by

T.B. Weston*

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ABSTRACT

Three experimental piezoelectric compositions in the lead titanate-lead zirconate series have been produced, using conventional ceramic fabrication techniques. Long-period grinding of the constituents in ball mills made it possible to employ sintering temperatures lower than those previously reported, but there was some loss of lead oxide during fabrication and impurity pickup during grinding was substantial. The finished ceramic samples proved difficult to pole, but development of a suitable poling technique yielded piezoelectric properties only slightly poorer than the best values reported in the literature for similar compositions, generally produced by more elaborate methods. Although some unexpected changes of composition during fabrication were observed, it was possible to draw some conclusions regarding the effect of minor chemical modification, including the addition of niobia, on the electromechanical properties.

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PROPRIÉTÉS ÉLECTROMÉCANIQUES DE TROIS COMPOSÉS CÉRAMIQUES EXPÉRIMENTAUX, À BASE DE ZIRCONATE DE PLOMB ET DE TITANATE DE PLOMB

par

T.B. Weston*

RÉSUMÉ

Trois composés piézoélectriques expérimentaux de la série du titanate de plomb et du zirconate de plomb, ont été élaborés suivant les procédés ordinaires de préparation des produits céramiques. Le broyage prolongé des constituants dans des broyeurs à boulets permet d'employer des températures de frittage inférieures à celles qu'on avait rapportées antérieurement, mais il y a eu perte d'une certaine quantité d'oxyde de plomb au cours de l'élaboration, et les impuretés absorbées au cours du broyage étaient assez abondantes. Il a été difficile d'en arriver à la polarisation des échantillons céramiques à l'état fini, mais la mise au point d'un procédé de polarisation convenable a permis d'obtenir des propriétés piézoélectriques à peine inférieures à celles des meilleurs produits semblables mentionnés dans les ouvrages de référence, à la différence toutefois que les produits en question avaient généralement été préparés suivant des procédés plus élaborés. Bien que certains changements imprévus dans la composition se soient produits au cours de l'élaboration, il a été possible de tirer certaines conclusions sur les effets de légères modifications chimiques, notamment l'addition de niobium, sur les propriétés électromécaniques.

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INTRODUCTION

Ferroelectric substances are characterized by a crystal structure containing an electric dipole which can be reversed by a suitable applied electric field. A single crystal of such a substance exhibits piezoelectric properties, but the magnitude of the effect may vary widely between different materials. Most ferroelectrics lose their polarity and hence their ferroelectric properties above some characteristic temperature, called the Curie point (1).

Certain ferroelectric substances, notably barium titanate, can be sintered at high temperature into the form of a ceramic. In such a ceramic the individual crystallites have essentially random orientation, and the ceramic as a whole is not piezoelectric. Application of a sufficiently high electric field for a suitable time causes a preferential alignment of the polarity of the individual crystallites in directions making the smallest possible angle with the direction of the applied field. After this process, known as "poling", the material has an over-all polarity and exhibits piezoelectric properties, although such properties are linear only over limited ranges of the input signal.

Actually, only a small number of compounds can be formed into a ceramic and subsequently acquire and retain a strong piezoelectric effect. Most of these compounds are known to have a distorted perovskite-type structure, ABO_3, in which the A ions occupy the corners and the B ions the centres of the unit cells, with the oxygen ions at the centres of the faces. In the case of barium titanate, for example, the barium ions occupy A positions and the titanium ions the B positions. In the ferroelectric compounds, the structure may adopt rhombohedral, tetragonal, or orthorhombic symmetry, changing to cubic above the Curie temperature.

The first important piezoelectric ceramic was barium titanate ($BaTiO_3$). Either alone or modified by suitable compositional additions (1-3), this material has been extensively used in electromechanical devices. The Curie temperature, however, occurs at about 120°C, and additional structural transitions, accompanied by discontinuities in properties, occur at about +10°C and -80°C. As these transitions can be shifted or suppressed only slightly by compositional modification without seriously reducing the piezoelectric response, the material is useful only over a limited temperature range.

More recently, it has been found that suitable combinations of the compounds lead zirconate ($PbZrO_3$) and lead titanate ($PbTiO_3$) have strong piezoelectric properties (4). These compounds form a complete solid solution system with two morphotropic phase boundaries (5). One of these, which is found near the composition containing 55 molecular per cent of the zirconate, separates a region of rhombohedral symmetry - for compositions richer in zirconium - from a region of tetragonal symmetry. Compositions

in the neighbourhood of this phase boundary exhibit piezoelectric response significantly higher than that observed in any material based on barium titanate. In addition, the Curie temperature lies above 300°C, and no other structural transitions have been observed, at least down to -150°C, except for the rather gradual changes associated with a slight temperature dependence of the phase boundary (6). The variation of properties with temperature might therefore be expected to be less than with barium titanate, and the useful temperature range greatly increased.

Lead zirconate-lead titanate piezoelectric ceramics, with properties superior to those of barium titanate in a number of important respects, have already been described in the literature (7-9) and are available commercially (10). It is felt, however, that further improvement in properties is possible, particularly if the specific requirements of one application, such as in underwater sound, are considered. In addition, the ceramics of this type, whose properties have been reported, have apparently been produced by methods basically similar to those used by Jaffe, Roth and Marzullo (4) in their pioneer work at the U.S. Bureau of Standards. This method involves the sintering of mixtures of lead, zirconium and titanium oxides at temperatures in excess of 1200°C to provide well-fired ceramics. At such temperatures the lead oxide in these compositions is highly volatile. Control of the lead content has therefore been attempted by firing in closed crucibles containing additions of lead-bearing compounds designed to provide an atmosphere of lead oxide vapour. It is believed, however, that such methods are not entirely satisfactory and that rejection rates are high. Finished ceramics of this type are therefore relatively expensive.

Preliminary X-ray diffraction investigations (11) indicated that reaction of the initial oxide constituents to form a perovskite solid solution might be completed at temperatures in the neighbourhood of 800°C, although sintering would not be satisfactory at this temperature. It was felt, however, that if particle sizes could be reduced to sub-micron ranges before the final forming and firing of the material, it might be possible to obtain well-sintered ceramics at temperatures substantially lower than those reported in the literature, or in shorter firing times. If such were the case, the loss of lead might be sufficiently low to have an insignificant effect on final properties, or at least to be easily corrected by adjustment of constituents.

Although there are several possible methods for producing particle sizes of the desired fineness, grinding in ball mills for sufficiently long periods is probably the most obvious. Unfortunately, wear of the ball jars and balls in such a process might add unwanted impurities to the constituents in sufficient quantity to cause detrimental changes in properties.

The principal purpose of the present investigation, therefore, is to examine the properties of lead zirconate-lead titanate ceramics produced by a method in which long-term ball-milling is a prominent feature. The

ceramics produced are analyzed for chemical changes, and the electromechanical properties are compared with those of similar compositions reported in the literature. As three different compositions are examined, some conclusions regarding the property changes induced by compositional modification can also be drawn.

MEASUREMENT OF THE PROPERTIES OF PIEZOELECTRIC CERAMICS

Properties Investigated

For any piezoelectric material the relationship between mechanical stress and strain, on the one hand, and electric field and displacement, on the other, can be completely described in terms of a suitable set of elastic, dielectric, and piezoelectric constants. These constants are defined and methods for their measurement described in the Standards on Piezoelectric Crystals of the Institute of Radio Engineers (IRE) (12-15). Because of the high degree of symmetry of a poled ceramic, the number of independent constants is considerably smaller than for a piezoelectric crystal of the most general class. Nevertheless, a number of measurements on samples of different shape and electrode configuration are required to determine their values. In an investigation of the present type, therefore, measurements are usually confined to the constants of greatest significance in possible applications of the material.

Whatever the symmetry of the individual crystallites, the symmetry elements of a poled ferroelectric ceramic, taken as a whole, are an axis of rotation of infinite order in the poling direction and the infinite set of all planes parallel to that direction as reflection planes (15). The material constants are therefore defined with reference to a coordinate system in which the "3" axis is aligned with the poling direction and the "1" axis may be aligned with any perpendicular direction. The numbers indicating the applicable directions appear, where significant, as subscripts in the symbols designating the various properties.

In many types of electromechanical transducers formed from piezoelectric ceramic material, the relationships between electrical signals in the poling direction and mechanical vibrations perpendicular to this direction are of special importance. In such a case the most significant parameters are:

piezoelectric strain constant	d_{31} meter/volt
piezoelectric voltage constant	g_{31} volt-meter/newton
elastic compliance at constant field	s_{11}^{E} meter ^{2}/newton

Poisson's ratio	σ^E	
dielectric permittivity at constant stress	ϵ_{33}^T	farad/meter
planar coupling factor	k_p	
transverse coupling factor	k_{31}	
electrical quality factor	Q_E	
mechanical quality factor	Q_M	

The above piezoelectric constants may be simply described by stating that the d_{31} constant indicates the strain in a free piezoelectric element produced by a given applied field or the charge produced by a unit force, while the g_{31} constant indicates the open circuit potential gradient produced by a given applied stress or the strain produced by a given charge density. They are not strictly independent, being related by:

$$d_{31} = \epsilon_{33}^T g_{31} \quad (1)$$

The elastic compliance listed above is frequently quoted as its inverse, the Young's modulus:

$$Y_{11}^E = \frac{1}{S_{11}^E} \quad (2)$$

The dielectric permittivity is more often given in terms of the relative dielectric constant, K_{33}^T, where:

$$\epsilon_{33}^T = K_{33}^T \epsilon_0 \quad (3)$$

and ϵ_0 = dielectric permittivity of free space
$= 8.854 \times 10^{-12}$ farad/meter.

An electromechanical coupling factor is related to the efficiency of energy conversion in the material, being defined as the square root of the ratio of the energy stored in mechanical form, for a given type of displacement, to the total input electrical energy. Of the two listed, k_{31} is appropriate for one-dimensional vibrations perpendicular to the poling direction, and k_p for two-dimensional planar vibrations perpendicular to the poling direction. They are related to each other and to the other parameters listed by:

$$k_p^2 = \frac{2}{(1-\sigma^E)} k_{31}^2 \quad (4)$$

$$d_{31}^2 = k_{31}^2 \epsilon_{33}^T s_{11}^E \quad (5)$$

The electrical and mechanical quality factors are inversely related to the magnitude of dielectric and mechanical losses in the material, which detract from the efficiency of a transducer. The electrical quality factor is the inverse of the dissipation factor, or loss tangent:

$$Q_E = \frac{1}{D} = \frac{1}{\tan\delta} \qquad (6)$$

A low value of dielectric loss is desirable in a transducer designed to detect low-level sound signals, e.g. a hydrophone, from the standpoint of thermal noise. For materials to be used in transducers handling large amounts of power, e.g. sound projectors, the value of the dissipation factor at high driving fields is particularly important. Too high a value of dielectric loss would result in excessive heating under load, followed by complete or partial depoling depending on the temperature attained and its proximity to the Curie temperature (3).

If Poisson's ratio is known, the values of all the other constants listed above can be deduced from measurements made on a ceramic sample in the form of a thin circular disk, provided with conducting electrodes covering the circular faces and poled in a direction perpendicular to these faces. Poisson's ratio can be obtained from measurements on thin square plates, which can be cut from the original disks.

The material constants or parameters are strictly constant only for fixed conditions of temperature and applied signal, and significant variations may be introduced by changes in these conditions. In addition, the values of the parameters will change with time after poling. As these effects may have an important bearing on the suitability of the material for any particular application, it is customary to include some studies of their magnitude in any evaluation of the properties of a piezoelectric ceramic.

Measurement of Dielectric Properties

The dielectric permittivity at constant stress is determined by measuring the capacitance of the sample on a suitable a-c bridge at a frequency that is low compared with the frequencies of all vibrational resonances. For a disk:

$$\epsilon_{33}^{T} = \frac{Ct}{A} \qquad (7)$$

whence, from Eq. 3,

$$K_{33}^{T} = \frac{Ct}{A\epsilon_0} \qquad (8)$$

where C = capacitance of disk (farads),
A = area of electrodes (meter^2),
t = thickness of disk (meters), and
$\epsilon_0 = 8.854 \times 10^{-12}$ (farad/meter).

Capacitance bridges commonly used for measurements at low frequency give, when balanced, a simultaneous indication of the dissipation factor at low voltages. For samples of the type considered here, a sample holder of comparatively simple design can be used, the high dielectric constant of the material making corrections for edge and ground capacitance unnecessary (16).

In the present investigation most of the capacitance measurements were made at 1000 cps with a General Radio Capacitance Bridge, Model 716C, connected to a suitable oscillator and detector. The nominal accuracy of this bridge is better than 0.5 per cent. A universal impedance bridge of slightly lower accuracy was employed to study the variation of dielectric properties with temperature.

The dielectric loss at high fields was measured at 10 kc with a substitution resonance bridge of the type described by Schofield and Brown (3). The voltage across the sample was indicated by an electrostatic voltmeter. The accuracy of these measurements is probably not better than $\pm$5 per cent. Limitations in the range of the bridge, together with the rapid heating exhibited by samples of high loss, make measurements practically impossible if the dissipation factor of the sample exceeds 0.1 (or 10 per cent). A material of such high loss would, however, be of little use in sound projectors.

Values of d-c resistivity were obtained by measuring the resistance of sample disks at a potential of 500 volts with a General Radio Megohmmeter, Model 1862B. For a disk with dimensions defined as before:

$$s = \frac{RA}{t}, \qquad (9)$$

where s = resistivity (ohm - meters),
R = measured resistance (ohms).

Because a number of errors are associated with these measurements, the values of resistivity obtained are considered only comparative.

Measurement of Elastic and Piezoelectric Properties

A piezoelectric element excited by an appropriate a-c signal exhibits various modes of vibration, each characterized by a series resonance frequency, f_s, and a parallel resonance frequency, f_p. In the case of a

circular disk of the type already described, the mode of lowest frequency is the radial mode. For this mode the disk can be supported by point contacts bearing lightly upon its centre without introducing appreciable loading. The frequencies of resonance can then be determined in a simple transmission circuit of the type shown in Figure 1.

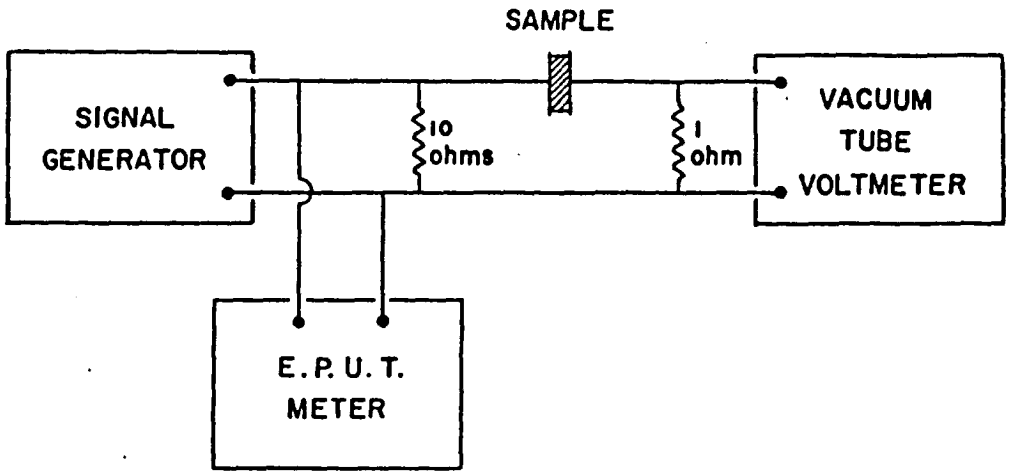

FIGURE 1. - Circuit for Measurement of Elastic and Piezoelectric Properties

As the frequency is varied in the neighbourhood of a resonance, maximum and minimum indications on the voltmeter correspond to the frequencies of minimum and maximum impedance, respectively f_m and f_n, for the sample. These frequencies differ by small amounts from f_s and f_p, respectively, but for samples of reasonably low loss and for suitably chosen circuit values the differences are negligible. Calculation of the values of the appropriate correction terms (13) (15) confirms that in the present case it is permissible to adopt the equalities:

$$f_s = f_m \quad , \quad f_p = f_n \quad , \quad \Delta f = f_p - f_s = f_n - f_m \qquad (10)$$

If the value of Poisson's ratio is known, the radial coupling factor can then be calculated from f_s and f_p for the radial mode:

$$\frac{k_p^2}{1-k_p^2} = \frac{(1-\sigma^E)\, J_1[\eta_1(1+\Delta f/f_s)] - \eta_1(1+\Delta f/f_s)\, J_0[\eta_1(1+\Delta f/f_s)]}{(1+\sigma^E)\, J_1[\eta_1(1+\Delta f/f_s)]} \qquad (11)$$

where J_0 is a Bessel function of the first kind and zero order,
J_1 is a Bessel function of the first kind and first order, and
η_1 is the lowest positive root of:

$$(1-\sigma^E)\, J_1(\eta) = \eta\, J_0(\eta). \qquad (12)$$

Young's modulus is given by the expression:

$$Y_{11}^E = \frac{1}{S_{11}^E} = \frac{\pi^2 d^2 f_s^2 (1-\sigma^{E2})\rho}{\eta_1^2} = \left(\frac{\pi N_d}{\eta_1}\right)^2 (1-\sigma^{E2})\rho \qquad (13)$$

where ρ = density of the material (kg/m^3),
d = diameter of disk (meters), and
$N_d = f_s d$ = disk frequency constant (cycle - meters).

The values of k_{31}, d_{31}, and g_{31} can then be calculated, using equations (4), (5) and (1) given earlier.

The expression for deriving the radial coupling factor is strictly valid only for an infinitely thin disk. For disks of finite thickness, the value of k_p obtained is higher than the true value for the material. Methods of correcting for finite thickness have been given by Baerwald (17). Consideration of the magnitude of the corrections applicable in the present case indicate an error of about 1 per cent. As such an error is negligible in comparison with others encountered in this type of investigation, it is not felt necessary to make corrections for finite thickness.

The value of Poisson's ratio cannot be determined with sufficient accuracy by measurements on a circular disk alone. Fortunately, the derived value of k_p does not vary very rapidly with σ^E, a change of about 30 per cent in the latter being necessary to alter the value of k_p by 1 per cent. In many investigations of this type, an assumed value of Poisson's ratio has been used. An actual measurement of σ^E would, however, be advisable in

cases where the values of d_{31} and g_{31} are of particular interest.

The most suitable method involves measurements on a thin square plate, electroded on the square faces and poled at right angles to these faces. For a ceramic sample of this type, the vibrational modes of lowest frequency are those known as extensional modes III and IV (14), for which the frequency constants are given by:

$$N_{III} = f_s^{III}\alpha = \frac{F_{III}}{2}\left(\frac{1}{s_{11}^E \rho}\right)^{\frac{1}{2}} \qquad N_{IV} = f_s^{IV}\alpha = \frac{F_{IV}}{2}\left(\frac{1}{s_{11}^E \rho}\right)^{\frac{1}{2}} \tag{14}$$

where α = length of plate side; whence $\frac{f_s^{IV}}{f_s^{III}} = \frac{N_{IV}}{N_{III}} = \frac{F_{IV}}{F_{III}}$.

Now F_{III} and F_{IV}, as well as their ratio, are functions of σ^E. Baerwald and Libove (18) have shown that, if the ratio F_{IV}/F_{III} is known, the value of σ^E is uniquely determined; they have given tables showing the numerical relationship directly. These tables have been reproduced, in part, in the IRE Standards (14), but, unfortunately, it is not made clear that the values are strictly applicable only to an infinitely thin plate. Proper application of corrections for finite thickness, as given by Baerwald and Libove, requires additional information difficult to obtain in a limited investigation of the present type. Consideration of the magnitude of the corrections indicates a probable absolute error of about 5 per cent in the value of σ^E due to omission of thickness corrections in the present case, but it would appear that the magnitude of the error would not change appreciably between members of a closely similar series of compositions. Values of Poisson's ratio determined in the above manner, even if uncorrected for finite thickness, could therefore be expected to give better comparative values of the calculated constants d_{31} and g_{31}, than an assumed constant value of σ^E.

Some of the difficulties mentioned above could be avoided by making measurements on samples in the form of long thin bars, but in practice these have been found much more difficult to form and to handle, particularly during poling, than circular disks and square plates.

The mechanical quality factor Q_M is obtained by measuring the minimum impedance $|Z_m|$ at fundamental radial resonance of a disk (15). After determination of f_m and f_n as previously described, a variable resistance is substituted for the test specimen and adjusted to give a current equal to the current through the specimen at f_m.

Then $$\frac{1}{Q_M} = 2\pi f_s |Z_m| (C_0 + C_1)\left(\frac{f_p^2 - f_s^2}{f_p^2}\right) \qquad (15)$$

or, effectively, $$Q_M = \frac{f_n^2}{2\pi f_m RC(f_n^2 - f_m^2)} \qquad (16)$$

where R is the resistance, measured as above, and $C = C_0 + C_1$ is the static capacity, as measured at low frequency.

As the accurate measurement of frequency is important in the above determinations, a Berkeley EPUT meter, reading frequencies up to 1 megacycle with a nominal accuracy of $\pm$ 1 cycle, was employed for this purpose in the present investigation.

EXPERIMENTAL PROCEDURE AND OBSERVATIONS

Preparation of Samples

The samples were prepared under the direction of Mr. I. F. Wright of the Ceramics Section from oxides having a stated minimum purity of 99 per cent, namely:

Fisher Certified	Lead Oxide	(PbO)
Baker Analyzed	Titanium Oxide	(TiO_2)
TAM CP	Zirconium Oxide	(ZrO_2)
Fansteel	Niobium Pentoxide	(Nb_2O_5)

The constituents were weighed on a balance having a maximum error of 0.2 per cent in the amounts necessary to give approximately 3-kilogram batches of the desired composition. The fact that the zirconium oxide may have contained up to 2 per cent of hafnium oxide - not usually considered an impurity - was disregarded.

After adding water, the constituents were mixed for 48 hours in one-gallon ball mills, made of a special high-alumina porcelain designed to give lower wear and lower silica contamination than conventional porcelain. The material was then dried to a water content of 6 per cent, pressed into large cakes, and sintered for 5 hours at 800°C in an electric furnace. The cakes were then broken through a 1/8-in. screen and ball-milled with water for a further 48 hours. After removing the water by filtering, the material was pressed into disks 1.73 in. in diameter in a steel mould at a pressure of 10,000 psi. These disks were placed in an electric furnace and the temperature raised to 875°C. After holding at this temperature for 1 hour, the disks were heated to the final temperature, held for 1/2 hour, and then

allowed to cool at the natural rate of the furnace.

The final firing temperatures were determined by firing small groups of samples at different temperatures and selecting the temperature yielding the highest density in the fired disks. The remainder of each batch was then fired as a whole at the selected temperature. The three compositions prepared are listed below with their respective firing temperatures:

(A)	55/45 mol per cent lead zirconate/lead titanate	1165°C
(B)	55/45 mol per cent lead zirconate/lead titanate with 1 wt per cent niobium pentoxide	1210°C
(D)	53/47 mol per cent lead zirconate/lead titanate	1165°C

The letter designations A, B, and D were used in laboratory records to refer to these compositions and will be retained throughout this report.

In the case of composition D the main group of disks was found after firing to have a lower density than had been expected on the basis of preliminary work. The disks were therefore returned to the furnace and heated to 1165°C to soak for a further half-hour period before being allowed to cool again in the normal manner. After this treatment the expected value of density was obtained.

Density determinations were made by weighing samples in air and water with a balance reading to 0.1 mg. The average density for all the samples in the main group for each composition was accepted as being representative of the composition.

The rough disks were lapped to make the faces flat and parallel and to bring the thickness to within 0.0001 in. of the nominal value. The diameters were made uniform to within 0.001 in. by grinding. Square plates were cut from disks and brought to the required size by similar methods. In this case the lengths of the sides were held uniform within 0.001 in. The nominal sizes of the two types of sample are as follows:

Circular:	diameter	d = 1.312(5) in. = 3.33(4)	cm
	thickness	t = 0.1875 in. = 0.476(2)	cm
Square:	side length	a = 0.787 in. = 2.00(0)	cm
	thickness	t = 0.0787 in. = 0.200	cm

After degreasing with trichloroethylene, conducting electrodes were applied by spraying with Dupont Conductive Silver #7095 (thinned to a density of 1.6 with butyl acetate) and firing in an electric furnace to a temperature of 600°C for 20 minutes.

Chemical Analysis

Samples of the original raw materials were checked for impurities by spectrographic analysis, as shown in Table 1. This analysis was carried out in the Mineral Sciences Division, as was the chemical analysis of the fired ceramics, shown in Table 2. The latter was made on a few disks of each composition broken into powder. The methods employed in the chemical analysis will not be considered in detail here, but were, in the main, gravimetric, and in accordance with the recommendations of Murphy, Clabaugh and Gilchrist (19). In this analysis any hafnium present would appear as zirconium.

The analysis shows that the fired ceramic contains a much larger amount of alumina than that found in the original raw materials. It seems clear that the increase shown is due to wearing of the ball mills and balls during fabrication.

The test for iron oxide was made because there was a possibility of contamination during fabrication, due to the proximity of other substances of high iron content. The figures show that there was significant contamination of composition D.

In Table 3 are given the values of two compositional ratios calculated from the chemical analysis, namely:

zirconium oxide/titanium oxide (mol per cent)
lead oxide/zirconium oxide + titanium oxide (mol per cent)

The molecular ratio lead zirconate/lead titanate, corresponding to the observed zirconia/titania ratio, is also included. Comparison with the intended ratios, also given in the table, shows that in compositions B and D some lead oxide has apparently been lost in firing. At the same time the ratio of zirconia to titania is decreased for these compositions. Composition A, on the other hand, reveals rather different behaviour, as both the lead content and the zirconia/titania ratio increased.

It is difficult to understand such differences in the behaviour of three closely similar compositions, prepared in essentially the same manner. The loss of lead oxide in composition B and D seems in reasonable accord with expectations, but it is not easy to account for the apparent shift in zirconate/titanate ratio, although consideration has been given to such contributing factors as moisture and volatile matter in the starting materials.

TABLE 1

Semi-Quantitative Spectrographic Analysis of Raw Materials

(Elements in Per Cent)

	Si	Mg	Fe	Bi	Cu	Ag
Lead Oxide	Tr	Tr	0.02	0.02	0.002	0.0008
Titanium Oxide	0.3	0.03	Tr	ND	ND	ND
Zirconium Oxide	0.4	0.03	Tr	ND	ND	ND

	Pb	Nb	Al	Ca	Ti
Lead Oxide	-	ND	ND	ND	ND
Titanium Oxide	0.07	0.08	0.3	ND	-
Zirconium Oxide	0.05	ND	0.1	0.4	0.03

Tr = Trace
ND = Not Detected

TABLE 2

Chemical Analysis of Fired Ceramics

(Constituents in Weight Per Cent)

Series	A	B	D
Nominal Composition (mol %)	55/45	55/45 with 1 wt % Nb_2O_5	53/47
PbO	67.37	65.93	66.44
ZrO_2	20.28	19.70	18.89
TiO_2	10.33	11.75	12.25
Al_2O_3	1.04	1.07	1.68
SiO_2	0.33	0.39	0.28
Fe_2O_3	0.05	0.06	0.32
Nb_2O_5		0.76	
Total	99.40	99.66	99.86

TABLE 3

Compositional Ratios Derived from Chemical Analysis

Series		A	B	D
Molecular Compositional Ratio, zirconate/titanate	Intended	55/45	55/45	53/47
	Observed	56/44	52/48	50/50
Molecular Compositional Ratio, zirconia/titania	Intended	1.22	1.22	1.13
	Observed	1.27	1.09	1.00
Molecular Compositional Ratio, lead oxide/zirconia + titania	Intended	1.00	1.00	1.00
	Observed	1.03	0.96	0.97

Measurements on Unpoled Samples

The capacitance of each sample was measured at room temperature and 1000 cps, using the instruments previously described. Average values of the dielectric constants are given later in the report, along with the values for poled samples.

The variation of the dielectric constant and the dissipation factor with temperature up to 500°C was determined on samples mounted singly in a small crucible furnace. Resistance measurements up to 200°C were made on samples immersed in a stirred bath of silicone oil.

The variation of the dielectric constant and the dissipation factor with temperature for each composition is shown in Figure 2. For composition B, the curves are similar to those found in barium titanate ceramics; a prominent peak in the dielectric constant, corresponding to the Curie temperature, is found at about 400°C, and a smaller peak is observed in the dielectric loss at the same temperature before the loss begins to rise rapidly above 425°C. In compositions A and D, however, the dielectric loss rises to such high values, in the neighbourhood of 400°C, that the bridge can no longer be properly balanced; and no subsequent decrease in capacitance or loss, allowing the Curie temperature to be defined, can be observed. The Curie point would, however, appear to lie in the neighbourhood of 400°C for both compositions.

In Figure 3 the logarithm of the resistivity is plotted against temperature. The observed values of resistance are subject to errors due to the shunting effect of the mounting arrangements and limitations in the range of the instrument, but the graphs are essentially linear over the range 75°C to 175°C. It is evident that the change in resistivity with temperature for composition B is very much less than for compositions A and D. Plotting the logarithm of resistivity against the reciprocal of the absolute temperature does not appear to give a linear relationship like that observed by Kulcsar (8). The errors mentioned may be large enough to obscure this relationship, however.

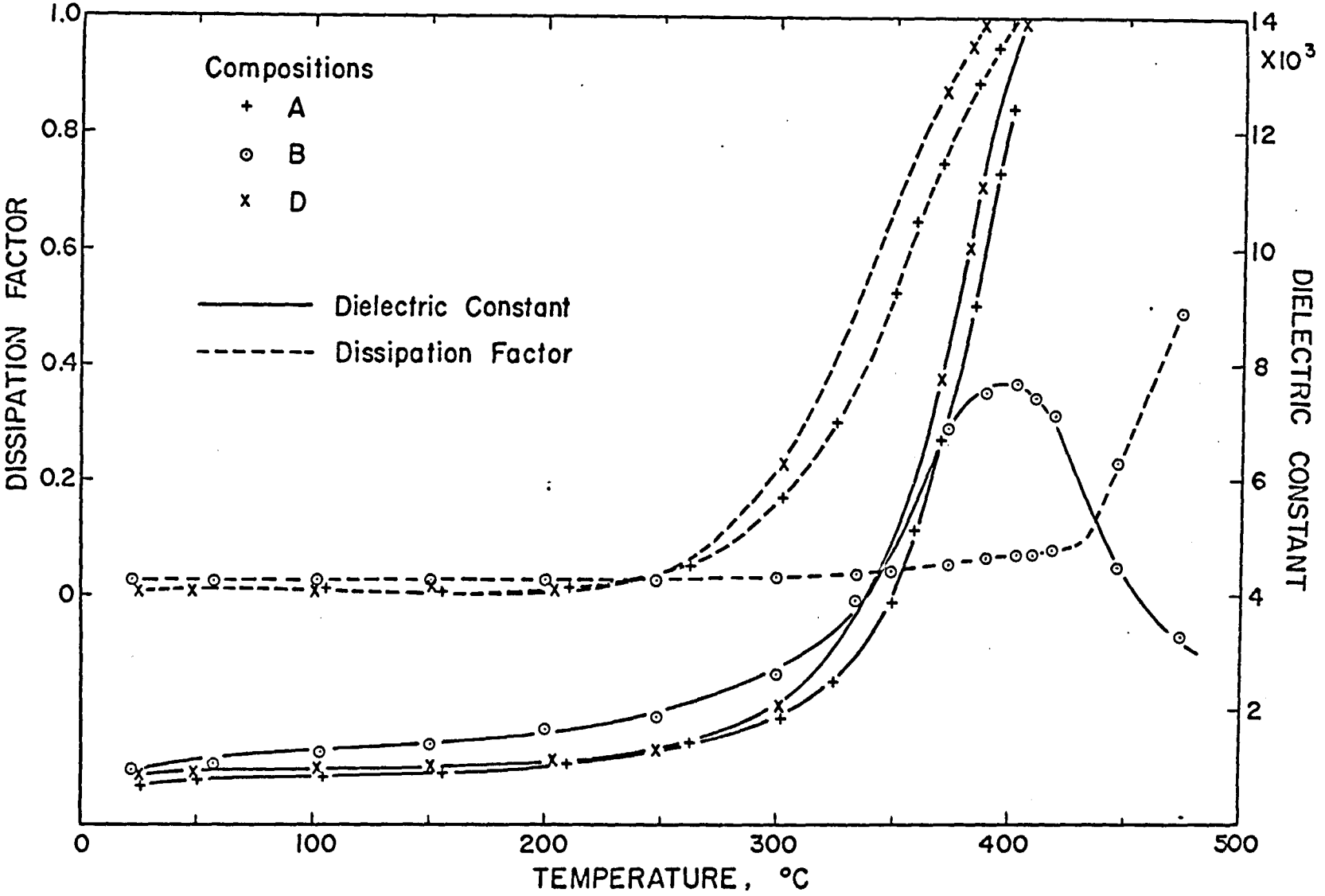

FIGURE 2. - Variation of Dielectric Properties with Temperature

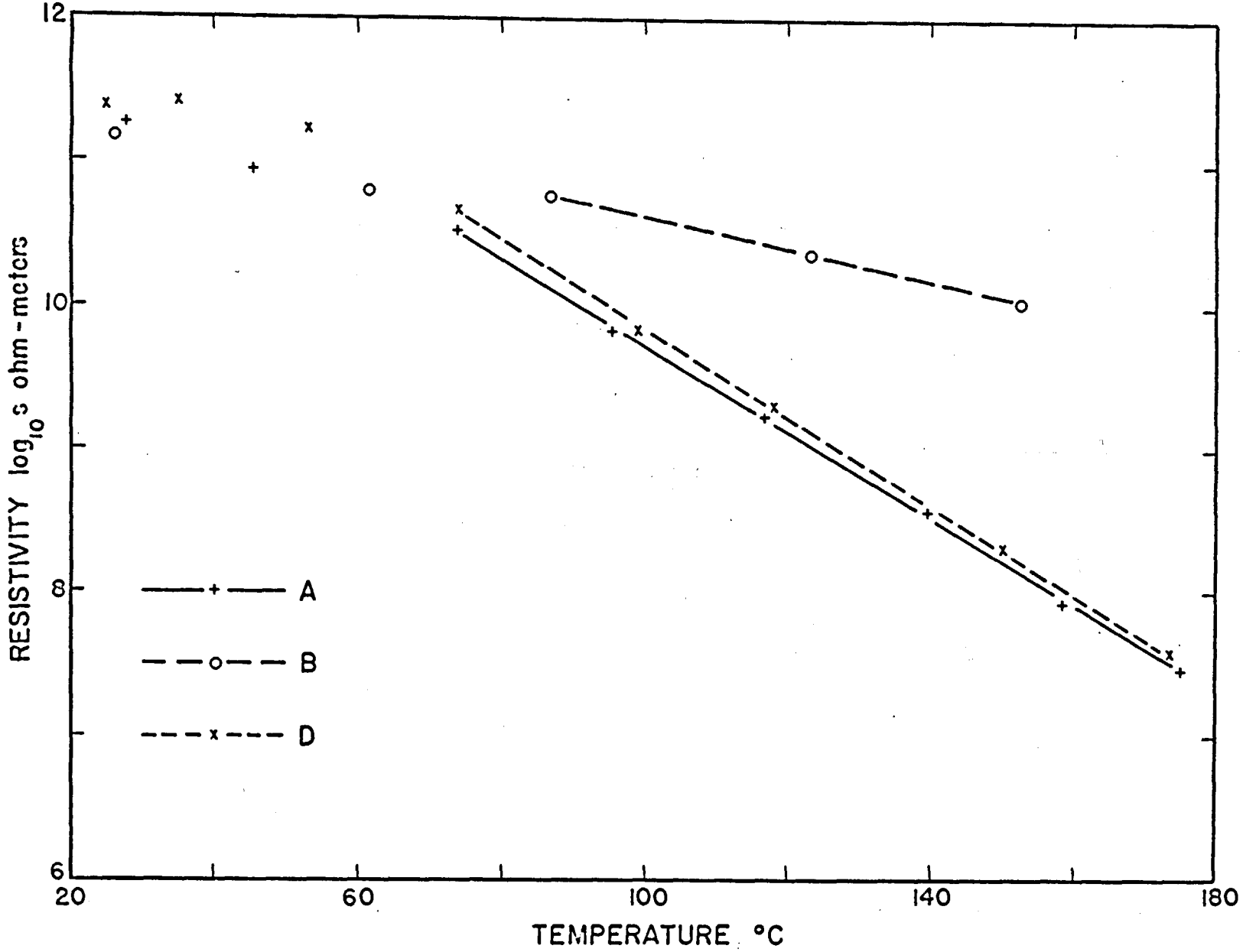

FIGURE 3. - Variation of Resistivity with Temperature

Poling

Although it is possible to pole a piezoelectric ceramic material by subjecting it to a sufficiently high electric field at room temperature, it was found at an early stage in the development of barium titanate ceramics that poling could be carried out more easily by applying the field at a temperature above the Curie point and subsequently cooling the material to a lower temperature before removing the field (20). This technique, unfortunately, is not possible with lead zirconate-titanate ceramics as the Curie point is too high and the dielectric strength of the material too low at elevated temperatures to withstand the necessary fields.

It was discovered, however, by Berlincourt and Brunarski (21), that at 100°C such materials could be satisfactorily poled by the application of fields of the order of 40 kilovolts per centimeter of thickness for a short time. The values of radial coupling factor obtained under these conditions were appreciably higher than could be achieved at room temperature, even with exposure to higher fields for longer periods. Fields of this magnitude approach the ultimate dielectric strength of the material so closely, however, that there is a strong possibility of voltage breakdown, followed by destruction of the sample in most cases. In general, lower fields will give lower values of coupling factor, as the latter approaches an ultimate or saturation value, characteristic of the field, for long poling times. Because of the usual variations in quality between individual ceramic samples, it is possible that with some materials the magnitude of the piezoelectric response attained, on the average, may depend on the proportion of samples which can economically be sacrificed in the poling process.

Initial attempts to pole the samples of composition A, using the temperature and field stated above, gave values of radial coupling about 15 per cent lower than those reported by Berlincourt and Brunarski. It was therefore considered necessary to carry out a number of poling experiments in order to determine the conditions for obtaining the highest possible response from the materials under study. In these experiments a sample, immersed in a stirred bath of silicone oil at the desired temperature, was poled in steps by applying the desired voltage for short periods. Between periods of exposure to the field, the sample was allowed to cool at room temperature for 15 minutes before measuring the response.

Curves showing the increase in radial coupling factor with time for several combinations of temperature and field are given in Figure 4. These curves are not exhaustive, but they illustrate sufficiently well the sort of behaviour exhibited by the experimental materials under investigation.

For composition A, it was found that a field of 40 kV/cm at 120°C gave the highest values of coupling consistent with the survival of most samples. Under these conditions, 95 per cent of the ultimate value of coupling could be attained within 12 minutes. Composition D was so similar to A in behaviour that it was not necessary to plot as many curves. For final evaluation of both materials the above combination of temperature and field was

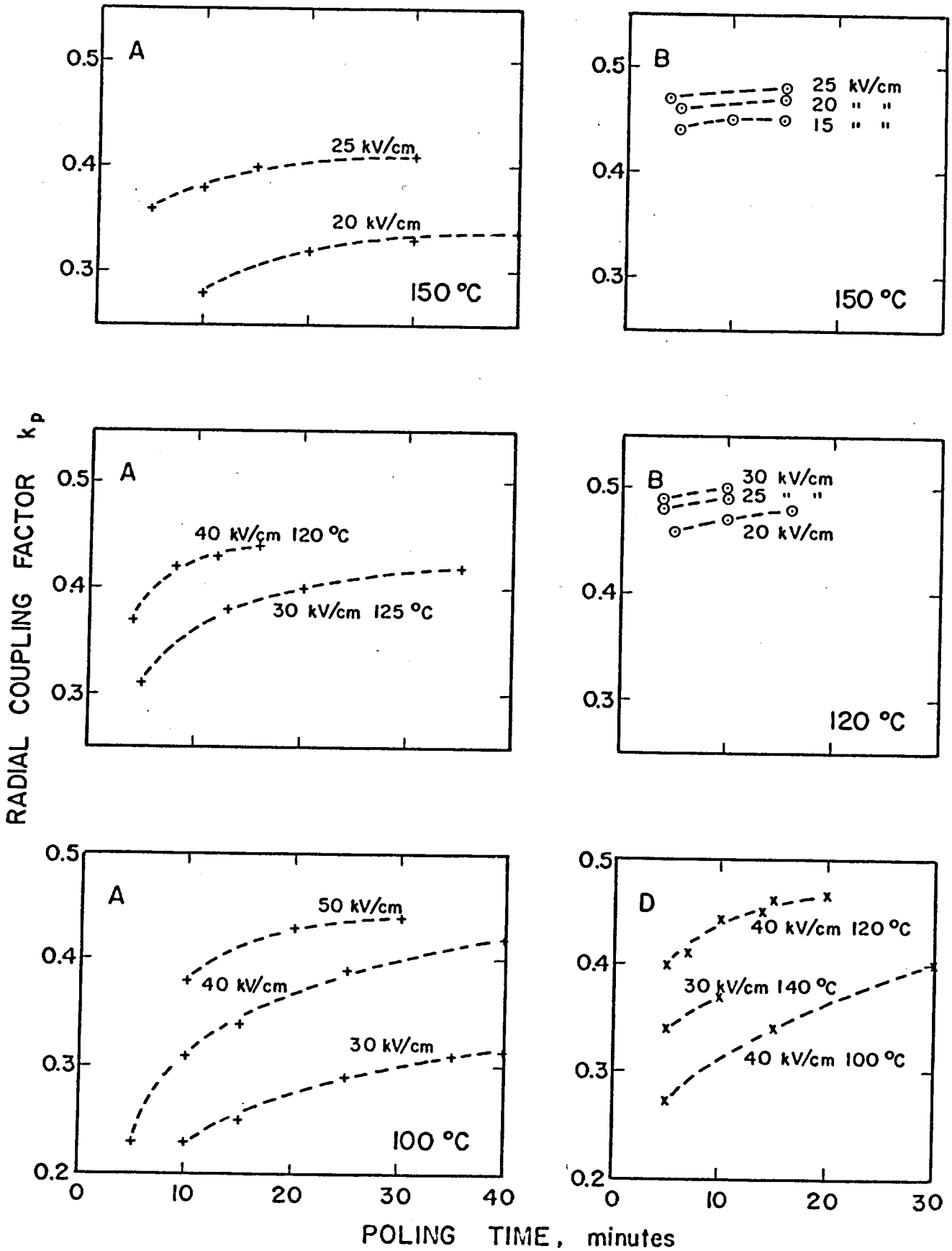

FIGURE 4.- Typical Poling Curves

employed in poling.

Composition B, however, exhibited rather different behaviour, the attainment of optimum coupling being less critically dependent upon temperature and field, and requiring shorter poling times. The curves for 150°C show values of coupling factor only slightly lower than those for 120°C, and a few samples poled at 100°C gave values similar to those obtained at 120°C. The curves for 5-kilovolt increments of poling field are also much more closely spaced than the corresponding curves for the other compositions. For convenience, composition B was poled for final evaluation at 120°C like the other compositions, but at a slightly lower field of 35 kV/cm, which nearly all samples could withstand. Under these conditions, 95 per cent of the saturation value of the coupling factor could be reached in less than 5 minutes.

A further difficulty was encountered with compositions A and D. If poled in steps, as previously described, total times of 20 minutes or more could be used, but if an attempt was made to pole a sample, by applying the field continuously for more than 10 minutes, shorting usually occurred. This effect may be caused by local heating in the sample, due to the current drawn during poling, which tends to increase with time because of the falling resistivity characteristic (Figure 3) unless all the heat generated can be removed. Instrumentation necessary to study this effect is, unfortunately, not yet available. Although it might be valuable for some purposes to know the maximum response attainable with a single stage of poling that the majority of samples could withstand, it was felt that the poling difficulties encountered with the present samples might be partly due to the relatively high impurity content, and that the ultimate or saturation values of coupling factor would give a better indication of the inherent properties of the compositions. For this reason the property values quoted later are based on samples that were poled several times in the course of experimental work for total times of at least 20 minutes. In addition, all were repoled 24 hours before final measurement for a further 5 minutes.

Measurements on Poled Samples

As a number of the samples originally produced were destroyed or damaged during the poling experiments, it was necessary to base final property values on four circular disks of each composition, supplemented by three square plates of each composition necessary to determine Poisson's ratio. The four disks in each group were repoled in rapid succession in the manner already described. Twenty-four hours after poling the following measurements were made at room temperature: capacitance and dissipation factor at 1000 cps and low field, dissipation factor at 10 kc and a field of 2 kV/cm (RMS), resonant resistance, and the frequencies of minimum and maximum impedance for the radial mode. The square plates were poled in two periods totalling 16 minutes. After 24 hours the frequencies of extensional modes III and IV were measured.

Following these measurements the properties of interest were calculated in the manner already discussed. Average values for the three compositions are given in Table 4.

Composition A (55/45 mol per cent lead zirconate/lead titanate nominal) and D (53/47 mol per cent lead zirconate/lead titanate nominal) are observed to have rather similar properties, as might be expected. Composition D has slightly higher dielectric constant, coupling factor, d_{31} constant and mechanical Q, but the g_{31} constant is lower. The difference in dielectric loss is, however, rather surprising. Composition B, nominally differing from A only by the addition of 1 wt per cent niobia, nevertheless exhibits significant changes in properties. The dielectric constant and d_{31} constant are doubled, but despite a higher coupling factor the g_{31} constant is lowered. The dielectric and mechanical losses are also much higher than in the other two compositions.

Aging

Changes in properties with time after poling were determined on groups of three samples of each composition, separate from those forming the basis of the 24-hour values quoted above, but poled in an identical manner. Measurements were made at suitable intervals between 1 day and 6 months after poling. Between measurements the samples were kept in a desiccator at room temperature.

In Figure 5, the dielectric constant, frequency constant, and radial coupling factor are plotted against the logarithm of the time in days. A straight-line relationship on such a graph indicates that the change in the property considered is a constant for each decade of time. This change can therefore be expressed as a percentage of the value at some fixed time, usually 1 day after poling. The graphs show that for composition B the aging at room temperature does follow a logarithmic law, at least for the period 1 to 100 days after poling. For compositions A and D, however, there is some indication of curvature, particularly in the case of the coupling factor. The straight lines on the graph are therefore drawn, somewhat arbitrarily, to indicate the slope over the two decades from 1 to 100 days only. It is evident that more frequent measurements and a longer study time are necessary to determine the aging behaviour accurately, but the present data are sufficient for the purpose of comparing the three compositions. It may also be noted that there are some differences between the 24-hour property values shown on the graphs and those quoted in Table 4. Variations in properties between individual samples are evidently sufficiently large that they cannot be disguised by averaging over such small groups. The differences are not serious, however, and the relative relationships between the three compositions are not changed.

From the graphs, and from the figures in Table 5, it will be evident that the addition of 1 per cent niobium pentoxide reduces the aging rates by a significant amount.

TABLE 4

Properties of Experimental
Lead Zirconate - Lead Titanate Ceramics

Series	A	B	D
Composition (mol % nominal)	55/45	55/45 + 1 wt % Nb_2O_5	53/47
Density (kg/m^3) x 10^3	7.62	7.52	7.65
Dielectric Constant (unpoled)	681	974	792
Dielectric Constant K_{33}^T	606	1259	859
Dissipation Factor (low field)	0.011	0.016	0.006
Dissipation Factor (at 2 kV/cm)	0.045	> 0.10	0.023
Disc Frequency Constant N_d (m/sec) x 10^3	2.34	2.11	2.26
Radial Coupling Factor k_p	0.45	0.52	0.47
Transverse Coupling Factor k_{31}	0.27	0.29	0.27
Poisson's Ratio	0.30	0.37	0.33
Young's Modulus Y_{11}^E (n/m^2) x 10^{11}	0.90	0.65	0.80
*Piezoelectric Constant d_{31} (m/V) x 10^{-12}	65	121	84
*Piezoelectric Constant g_{31} (V.m/n) x 10^{-3}	12.2	10.8	11.1
Mechanical Quality Factor Q_M	242	83	307

Temperature, 26 $\pm$1 °C.

Measurements made 24 hours after poling.

*The values of the piezoelectric constants should be preceded by algebraic signs, significant principally in static phenomena, which were not determined in this investigation. For piezoelectric ceramics of the type considered here, the sign is believed to be negative for both d_{31} and g_{31} (9).

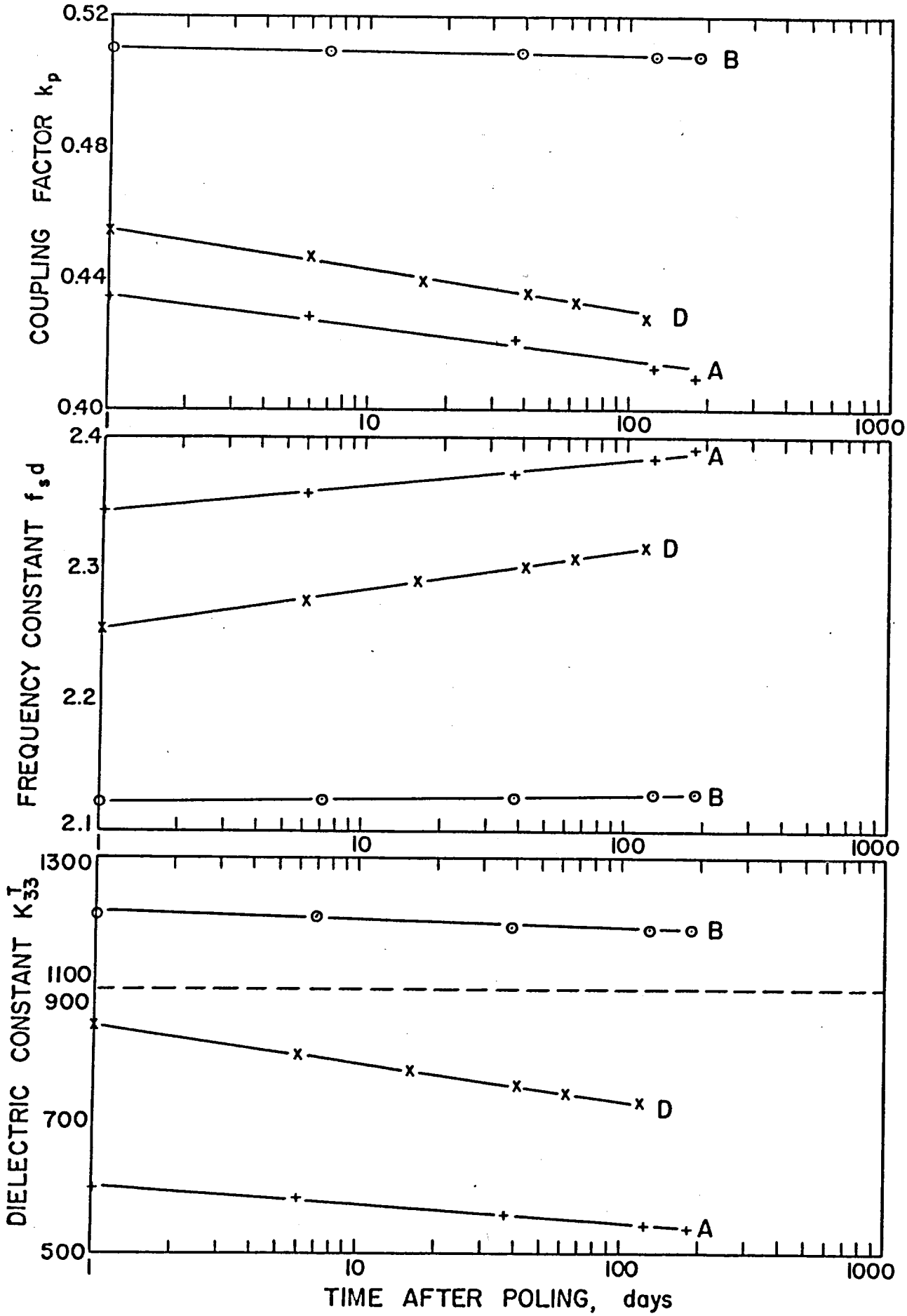

FIGURE 5. - Variation of Properties with Time

TABLE 5

Aging Rates for Experimental Compositions

(Per Cent Change Per Time Decade)

1 to 100 Days after Poling

Series	A	B	D
Dielectric Constant K_{33}^T	4.8	1.1	6.6
Coupling Factor k_p	2.3	0.3	2.6
Frequency Constant N_d	0.9	0.2	1.3

DISCUSSION OF RESULTS

It has been noted in the introduction that the main purpose of the present investigation is to test the suitability of a particular method of producing lead zirconate - lead titanate ceramics. As some information is already available in the literature about the properties of such materials, it would seem that a comparison with properties already reported would give a good indication of the success of the procedure. In Table 6 (a) are given values of some of the material parameters for a series of lead zirconate - titanate compositions, as reported by Berlincourt et al. (9). Part (b) of the table gives corresponding values for a similar series of compositions containing 1 wt per cent of niobia, as reported by Kulcsar (8), and part (c) the values for the present compositions.

Exact comparisons are difficult because of uncertainties, previously indicated, as to the exact compositions of the materials studied in the present investigation. Some further light can be thrown on this problem, however, by examining the values of dielectric constant before and after poling, as shown in Table 6. In unmodified compositions with zirconate/titanate molecular ratios lower than 51/49, the dielectric constant increases after poling, while for higher ratios it decreases. Composition D would therefore appear to lie below this limit, and composition A above. In materials containing 1 wt per cent of niobia, the corresponding limit would appear to lie near the 55/45 composition. Values in Table 6 indicate that the compositional ratio for the B material is lower than this, as the dielectric constant increases after poling.

TABLE 6

Comparison of Properties of
Lead Zirconate - Lead Titanate Compositions

(a) Unmodified (after Berlincourt et al. (9))

Compositional Ratio (mol %)	50/50	52/48	54/46	56/44	58/42
*K (unpoled)	720	890	730	590	510
K_{33}^T (poled)	846	730	450	423	397
k_p	0.40	0.53	0.47	0.45	0.43
d_{31} (meter/volt) x 10^{-12}	70	94	60	54	49
g_{31} (volt-meter/newton) x 10^{-3}	9.4	14.5	15.1	14.5	13.9

(b) With 1 wt % Niobia (after Kulcsar (8))

Compositional Ratio (mol %)	50/50	52/48	54/46	56/44	58/42
K (unpoled)	879	985	1051	818	713
K_{33}^T (poled)	1041	1200	1296	745	630
k_p	0.42	0.45	0.54	0.53	0.49
d_{31} (meter/volt) x 10^{-12}	82	97	128	93	75
+g_{31} (volt-meter/newton) x 10^{-3}	8.9	9.2	11.2	14.1	13.4

(c) Present Compositions (from Table 4)

Series	A	B	D
K (unpoled)	681	974	792
K_{33}^T (poled)	606	1259	859
k_p	0.45	0.52	0.47
d_{31} (meter/volt) x 10^{-12}	65	121	84
g_{31} (volt-meter/newton) x 10^{-3}	12.2	10.8	11.1

*Taken from a graph.

+Calculated from other figures reported.

It would therefore appear that for compositions B and D the compositional shift indicated in Table 3 is substantially correct in direction and magnitude. On this assumption the properties of these two compositions are closely comparable with those shown in Table 6. The compositional behaviour of the A material is, however, not clarified by the above analysis. Its properties are, nevertheless, closely comparable with those given by Berlincourt for materials in the same compositional range, except that the g_{31} constant is somewhat lower.

Shifts in the zirconate/titanate ratio after firing have apparently not been reported in the literature, and may be peculiar to the method of fabrication employed here. Unfortunately no indication is given, in either of the reports cited above, that the nominal compositions listed were actually confirmed by chemical analysis. Changes of the type indicated in the present investigation will obviously increase the difficulty of reproducing intended compositions precisely.

For similar reasons it is difficult to come to firm conclusions about the magnitude and effect of lead loss. Although firing temperatures were somewhat lower than those previously reported (4) (7), a small but measurable loss of lead oxide was observed in compositions B and D. The properties are, however, not appreciably poorer than those listed in Table 6. The reports, from which Table 6 was derived, unfortunately do not state whether the lead loss, if any, was actually determined for the samples examined. In the text of his patent, however, Kulcsar (22) notes the importance of this problem.

Notwithstanding the difficulties discussed above, it seems clear that the properties of the experimental materials under study are very little inferior to those previously reported in the literature. That this is so in spite of the large alumina and silica impurity content is particularly encouraging. The significant iron oxide impurity in composition D does not seem to be as seriously detrimental as had been expected.

The apparently different changes in composition exhibited by materials A and B make the effect of the niobia addition less clear than had been hoped. The changes in properties are, however, in general agreement with those shown in Table 6, which indicates an increase in dielectric constant and d_{31} constant over a considerable range of compositions. The maximum values of d_{31} and g_{31} do not occur at the same compositional ratios in both unmodified and niobia - modified materials, and maximum values of g_{31} are slightly higher in the unmodified series. The increase in dielectric and mechanical losses with addition of niobia is quite evident from the present results, however, as is the improvement in aging behaviour. The modified material is also somewhat easier to pole, and to this is obviously related the fact that the d-c resistivity at elevated temperature is much higher than for the plain lead zirconate - lead titanate ceramics.

CONCLUSIONS

The results of the present investigation indicate that lead zirconate - lead titanate piezoelectric ceramics of reasonably good properties can be produced by fairly conventional ceramic fabrication methods. It would appear, however, that further improvement in properties could only be obtained by the adoption of more specialized methods designed to overcome some of the difficulties encountered.

The most serious problem is concerned with the long period of ball-mill grinding required to reduce the constituents to a sufficient degree of fineness to permit rapid sintering. Although this long period was successful in the intended purpose of reducing the loss of lead oxide to small values, the significant quantity of impurities thereby introduced was undoubtedly instrumental in reducing property values to a level somewhat below that reported in the literature for similar compositions. As it is possible that this difficulty may be overcome by using pneumatic methods of grinding, investigations employing such methods are already in progress.

A second difficulty is the appreciable change in chemical composition apparently brought about in the fabrication process. No completely satisfactory explanation for this change could be found, although a more careful analysis of the original constituents might have thrown some additional light on the problem. Because significant changes in properties accompany comparatively small changes in composition, it will obviously be necessary to establish better control over final composition than was achieved in the present investigation.

The reasonably good results obtained, despite the difficulties mentioned above, give some measure of confidence that the adoption of other fabrication methods currently under investigation will yield a significant improvement in properties.

ACKNOWLEDGEMENTS

The investigations described above are part of a continuing program of study carried on at the request of the Naval Research Establishment, Dartmouth, Nova Scotia. The advice and encouragement of officers of that Establishment, in particular Dr. D. Schofield and Mr. R.F. Brown, are hereby acknowledged. Mr. I.F. Wright has had general supervision of the program within the Mineral Processing Division, particularly with regard to ceramic studies and processing methods. Mr. R.M. Buchanan carried out X-ray diffraction studies to determine the temperatures at which the raw material oxides reacted to form the desired zirconate-titanate compounds. Chemical and spectrographic analyses were carried out in the Mineral Sciences Division, and lapping of the samples in the Naval Section of the Mines Branch.

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