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AGING OF THE DIELECTRIC PROPERTIES OF SOME PEROVSKITE CERAMICS

BY

HECTOR TROCHE-MALDONADO

A

THESIS

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ABSTRACT

The effect of aging upon the dielectric constant and the dissipation factor were investigated for a number of lead titanate zirconate ceramics of varying composition. The ceramics investigated have a perovskite type structure. The materials chosen all have tetragonal symmetry at room temperature, but are close in composition to materials of rhombohedral symmetry.

Empirical relations were determined for each specimen giving the rate of aging of the dielectric constant (K) and loss factor in terms of the frequency (f) and the elapsed time (t). The range of frequency was 1 kcps to 1 mcps; the range of elapsed time was from 2 hours to 2000 hours. The general expression for the change in dielectric constant with time was found to be

$$dK/dt = \frac{(A \log f - B)}{t} ,$$

where A and B are positive constants, which were different for every one of the samples. During the period of measurement the aging rate for dielectric constant was greatest at low frequencies.

The compositions showing greatest aging were those closest to the tetragonal-rhombohedral phase boundary. These were also the compositions with the highest dielectric constants and the lowest crystallographic c/a ratios.

No frequency dependence of aging has been reported before for perovskites ceramics. The time dependence found in this investigation is similar to those reported by other investigators previously for different ferroelectric materials.

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INTRODUCTION

It has been observed by several investigators that the dielectric constant and the dissipation factor of ferroelectric titanate ceramics decrease gradually with time after the samples are cooled through the Curie point. This aging process has been observed also in other types of ferroelectric ceramics and for the case of other physical properties. In previous investigations the phenomena have been studied usually at a particular frequency.

The transition at the Curie point for perovskite type ferroelectrics is accompanied by a change in the unit cell of the crystal during the cooling process from cubic to tetragonal. For a crystallite embedded in an elastic medium smaller stresses will develop, if the change in the overall shape is as small as possible. The shape change of the crystallite can be reduced by crystallographic twinning(1). Twinning can occur by formation of domains at 90° or 180° to each other.

As a consequence of the tendency toward minimization of the over-all energy of the crystal, a gradual localization of domain walls will occur at locations where they have a minimum potential energy. The domain walls are fastened in their new locations (possibly by imperfection in the crystal) and the mechanical stresses in their vicinity are reduced to a minimum. As a result some regions of the crystal may orientate more readily under the influence of an external applied field than others.

Whenever any drastic rearrangement of the domain pattern occurs, an aging process begins. The rearrangement may consist of cooling through the Curie point or of reorientation of domains by electrical or mechanical stress. The aging is of a magnitude easily observable in bridge measurements of dielectric constant.

The purpose of this investigation is to determine how this aging mechanism varies with the frequency, for ferroelectric ceramics of different composition, at constant temperature. It is obvious that aging effects are of great importance to the practical application of ferroelectric materials. It is also felt by some investigators(2) that measurements of the dependence of aging with the frequency may help to gain additional insight into the aging mechanism, which most authors believe is due to the movement of domain walls from metastable positions to more stable ones(2, 3, 4).

The compositions studied were solid solutions of lead titanate and lead zirconate. The properties of such solid solutions were originally described by Shirane, Suzuki, and Takeda(5). Although PbZrO_3 is antiferroelectric, all its solid solutions, containing more than 10 mole per cent PbTiO_3 , are ferroelectric. Solid solutions containing less than 45 mole per cent PbTiO_3 are rhombohedral, while those containing more than this amount are tetragonal, isostructural with both PbTiO_3 and BaTiO_3 . Their Curie temperature varies from 220° - 490°C , depending on composition. For the phase diagram of $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ refer to Figure 1.

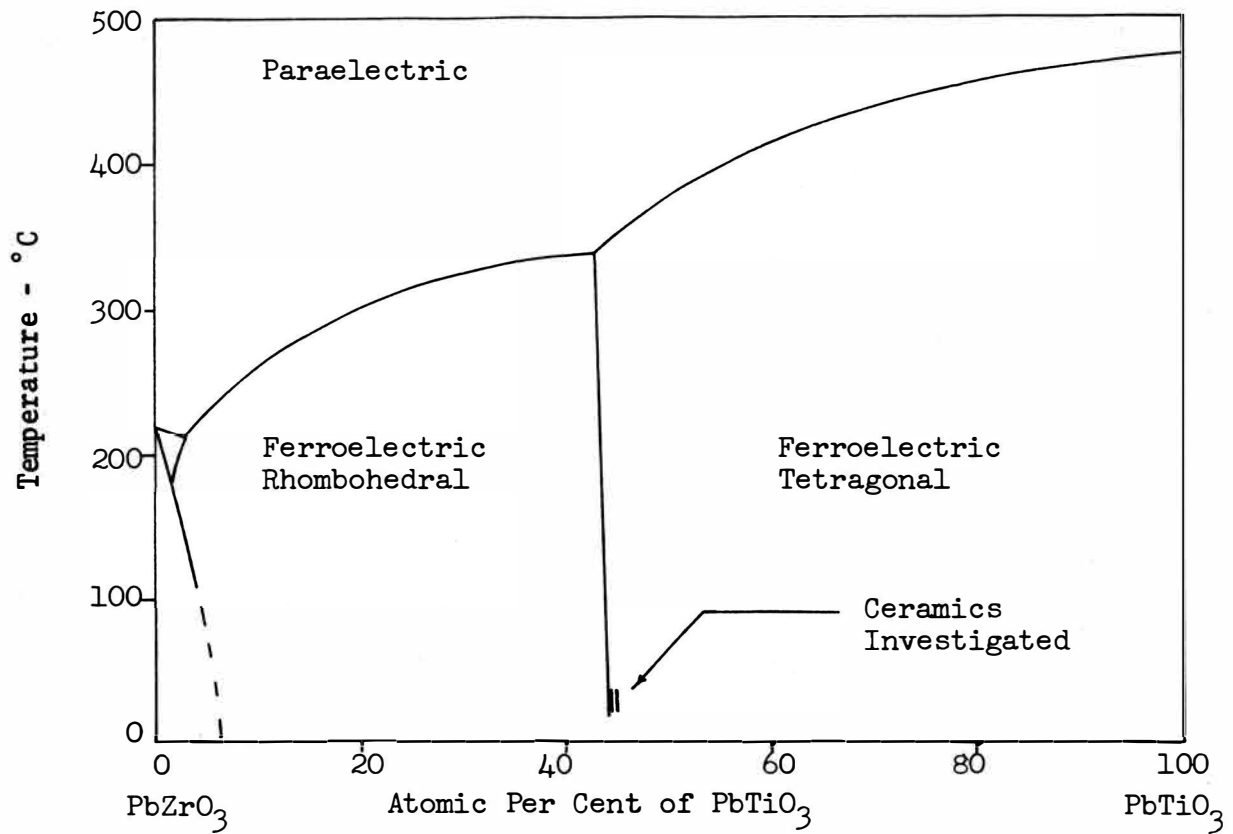


Figure 1. Phase Diagram of $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ (1)

The specimens used in this investigation have small amounts of strontium partially replacing lead near the morphotropic boundary. F. Kulcsar(6) reports the following important physical changes brought about by this substitution:

- a. Substantial increases in dielectric constant accompanied by some lowering of the Curie temperature.
- b. The morphotropic boundary is moved somewhat toward the rhombohedral side.
- c. A decrease in the distortion from cubic symmetry.

The last item may be important to the aging effect, because of the primary role that tetragonalization plays in the formation of stresses in the ceramic.

The samples used in this investigation were X-rayed by W. R. Cook(7) and found all tetragonal, with the ratio of the axial lengths (c/a) changing with composition as follows:

Composition	c/a
No. 1 - $(\text{Pb}_{0.94} \text{Sr}_{0.06})(\text{Ti}_{0.49} \text{Zr}_{0.51})\text{O}_3$	1.022
No. 2 - $(\text{Pb}_{0.94} \text{Sr}_{0.06})(\text{Ti}_{0.48} \text{Zr}_{0.52})\text{O}_3$	1.022
No. 3 - $(\text{Pb}_{0.94} \text{Sr}_{0.06})(\text{Ti}_{0.47} \text{Zr}_{0.53})\text{O}_3$	1.020
No. 4 - $(\text{Pb}_{0.94} \text{Sr}_{0.06})(\text{Ti}_{0.46} \text{Zr}_{0.54})\text{O}_3$	1.019

R. Cook suspects that the lack of linearity between the first two samples is probably due to inaccuracy in the measurements.

REVIEW OF LITERATURE

A. Historical

The first observation of the aging phenomenon was reported in 1948 by B. H. Marks(8). While trying to develop a capacitor of high dielectric constant from barium titanate, he tried to broaden the peak of the curve of the temperature vs. dielectric constant curve to avoid excessive changes on the working-temperature range. This was accomplished, but he observed a considerable decrease in the peak values of the dielectric constant with time. The effect was greater for materials of higher dielectric constants. In the same year, E. N. Bunting(9) studied the effect in the ternary system CaO-BaO-TiO_2 and found that certain compositions also showed a decrease of the power factor with time. According to McQuarrie and Buessem(2) (1954, p. 403) "the dissipation factor of barium titanate also decreases with time, the decrease being much greater (percentage-wise) than the decrease in capacitance." This quotation refers to reports made by Russian investigators in 1952. Similar results for barium titanate and related ferroelectric ceramics, including aging of other physical properties, have been reported since then(2, 3, 4, 10, 11, 12).

B. Ferroelectricity (Brief Discussion)

The aging process is associated with the ferroelectric state of the so-called ferroelectric materials. The following outstanding

properties are associated with ferroelectrics:

- a. There is a phase transition from the nonpolar (paraelectric) phase to the polar (pyroelectric) phase. This means that a temperature exists (an exception was reported by G. Goodman in 1957(13)) known as the Curie point, at which the transition occurs.
- b. They show spontaneous polarization, i.e. polarization that occurs spontaneously without the application of an external electric field.
- c. They show hysteresis effects between polarization and applied electric field.
- d. The direction of the spontaneous polarization may be changed by an external electric field.

Four groups of ferroelectric compounds are:

- a. Rochelle salt (K Na tartrate).
- b. The monohydrates of some mixed tartrates.
- c. Mono-potassium, di-hydro phosphate and some isomorphous compounds with related structures.
- d. Barium titanate and a number of compounds with related structures.

The samples used in this investigation possess the perovskite structure characteristic of the barium titanate group(1). Transitions of ferroelectric members in this group, at the Curie point, involve a change of the crystal structure from cubic at high

temperature to tetragonal in the low temperature phase. The direction along which the spontaneous polarization appears becomes the c-axis of the tetragonal crystal. The spontaneous polarization is considered equally probable for the six possible directions of the cubic structure.

According to Megaw(1) it seems that the recurrent feature in all perovskite-type compounds, which show ferroelectricity, is a polyhedron of oxygen atoms with a strongly bound metal atom slightly displaced from its geometrical centre. X-ray measurements by Evans and Hutner(14) in 1951 have shown, however, that the oxygen nuclei do move much more than the titanium nuclei, making it more reasonable to suppose both types of displacements responsible for the rise of the dipole moment of the unit cell when going to lower symmetry.

A theory which associates the phenomenon of ferroelectricity in pseudo cubic crystals to the normal modes of vibration was discussed by W. Cochran(15) in 1959. The conditions for a ferroelectric transition appear to be a problem in lattice dynamics, the transition being associated with the instability which arises when the frequency of one of the modes of vibration approaches zero. The theory has been extended to include ferroelectric cubic crystals, and shows that one of the modes of vibration in barium titanate should reach an abnormally low value (10^{11} c.p.s.) near the Curie temperature.

C. Aging:

Since the first observation of the aging effect, different theories have been proposed to account for the phenomenon. Most investigators seem to agree in a relaxation type mechanism in terms of domain wall motion. A full understanding of the aging process and a quantitative treatment will probably be possible after a better understanding of the ferroelectric polarization mechanism in polycrystalline materials. A discussion of some of the proposed theories follows:

The first qualitative and quantitative treatment of the aging phenomena is due to W. P. Mason(4) in 1954. This report has been unfavorably commented upon in some respects by Plessner(3) and Misarova(10).

In order to see if the decrease of the physical properties with time was somehow connected with a process having an activation energy, Mason determined experimentally two sets of aging curves for polarized barium, calcium, lead titanate ceramic compositions at the temperatures of 25°C and 70°C. He noticed that all the aging characteristics occur much more rapidly for the higher temperature. The activation energy was determined by the formula

$$(1) \quad H = \log_e \frac{t_2}{t_1} \times \frac{RT_1T_2}{T_2-T_1}$$

where t_1 and t_2 are the times required to complete a given portion

of the entire aging cycle at the absolute temperatures T_2 and T_1 and R , the gas constant. The determination of H gave a value of 19 kilo-calories; this value increased for higher temperatures. The same specimens were depolarized and reaged at 100°C and measurements made after the ceramic had cooled to room temperature showed that this alternating high and low temperature causes a faster aging than high temperature alone.

By a formal treatment, involving a generalized elastic enthalpy function, Mason connected the permittivity and the piezoelectric and elastic constants with the permanent polarization (P_0) of the ferroelectric ceramics. The aging of all of these physical properties was attributed to a decrease in P_0 , whose connection with the investigated parameters was determined empirically. Mason derived theoretically an equation which shows that the vanishing of P_0 would necessarily involve a decrease in the permittivity, power factor, and electromechanical coupling factor.

The aging of P_0 was visualized by Mason as coming from the relaxation of stresses which occur during cooling through the Curie point, poling or orientation process. With no field present P_0 will apply to individual grains, the average over the ceramic being zero.

In the unpolarized ceramic there is no resultant polarization, but the arrangement of domains in a single ceramic grain is not balanced. Thus, there is a resulting polarization in individual

grains, although they balance as a whole. Initially, then, the dielectric constant is higher but decreases as the domain walls equalize their position in the direction of smaller resultant polarization in each grain.

The average size of a ceramic grain reported by Mason was about 4 microns in diameter. Due to irregularities and residual stresses in the grain, the areas of the individual domains are, in general, not equal when they are formed, and mechanical stresses exist which tend to equalize the areas in the course of time. Mason gives a mathematical discussion of the process of domain wall motion, where he shows that the aging process is consistent with an equalizing of areas of the domain brought about by thermal energy biased by stored up stresses. In the relaxation of stresses Mason considered that the domain walls move in steps of one lattice unit, the motion being induced by an activation energy (E), of 19 kilo-calories per mole. Since the stress is proportional to the square of the distance of the domain wall from its equilibrium position, the position of the wall is determined by a relation of the form $B/(1 + At)$. The aging of the physical properties measured follow a similar relation. The aging of the permittivity, for example, is given by the expression

$$(2) \quad \epsilon - \epsilon_0 = B/(1 + At) \quad , \text{ where}$$

ϵ_0 corresponds to the fully aged value, A and B are constants and t is the time.

W. Plessner(3) has indicated that his experimental results cannot be fitted to an equation of the form $B/(1 + At)$, while adding that Mason's results can be fitted reasonably well to a $\log t$ law. He considers that a difference of 1.3 in the slopes of the E vs. $\log t$ plot at 25°C and 70°C does not allow a determination of the activation energy. Further, he adds that Mason gives no physical explanation of the dependence of permittivity and elastic constant on P_0 . The figure for the activation energy of 19 kilo-calories per mole does not fit into the type of domain wall motion envisaged by Plessner.

A. Misarova(10) believes that a hypothesis like that of Mason, which considers an ideal crystalline lattice, cannot be used to explain the nature of the aging process in barium titanate. For an actual crystal she attributes the aging of the permittivity not only to shifting of domain walls but also to a decrease in the ionic part of the permittivity due to the localized defects.

M. C. McQuarrie and Buessem(2) do not suggest any precise picture of the aging mechanism, although they indicate that it seems probable that it is connected with domain processes. They discuss the possibility of considering the aging process as a relaxation phenomenon. They indicate that, if this is the case, one has to account for the observed difference in relaxation times of the aging process and the ferroelectric polarization. The variation may indicate that the aging process is different in

nature from the ferroelectric polarization; i.e., that it consists in the deepening of the potential wells of the domain walls by diffusion processes or mechanical creep (progressive elongation with time under conditions of constant stress which depend on the load, temperature, the dimensions and the material). They suggest, then, that the relaxation times would be the ones connected with diffusion or creep. However, their experimental results with regard to the effect of calcium titanate additions on the aging rate of barium titanate, and the variation of the c/a ratio of the unit cell with the mole per cent calcium titanate present, shows a dependence of aging on the c/a ratio, the rate decreasing as c/a increases. This dependence of aging suggests that it is a movement of domain walls from metastable positions to more stable ones. Measurements of the activation energy in the case of aging cannot be made by measuring the temperature dependence, because the c/a ratio and with it the activation energies depend strongly on temperature.

Theoretical considerations by McQuarrie and Buessem indicate ((2), p. 406) that, "since the aging rate (percentagewise) of the dissipation factor is observed to be 4-5 times the aging rate of the dielectric constant and since all the polarization mechanisms with relaxation frequencies from infrared to the measuring frequency contribute to the dielectric constant, while only those with relaxation frequencies in the neighborhood of the measuring frequency contribute to the dissipation factor, it can be concluded

that the mechanisms with relaxation frequencies in the very high frequency range must have a definite smaller aging rate."

Another theoretical approach to the aging problem was given by K. W. Plessner(3) in 1956 for ceramic barium titanate. Plessner visualized the randomly oriented grains and the domains within the grains of ferroelectric ceramics as effectively clamping one another. Following an analysis by Devonshire (1951), he considered that the average permittivity of randomly oriented free grains (3100) will be reduced by a factor of ten when the grains are combined to form a dense ceramic. He indicated that the observed value of 1500 may be accounted for by postulating a large contribution from the motion of domain walls under the influence of an external applied field. Following an argument analogous to that by Street and Wooley (1949), where a relaxation process was assumed in connection with the phenomenon of magnetic viscosity (persistent changes in magnetization too great to be accounted for by eddy current formation), Plessner determined an equation for the time decrease of permittivity,

$$(3) \quad \epsilon = \epsilon_0 - ST \log t$$

where ϵ_0 and S are constants, T is the absolute temperature, and t the time. He determined theoretically the range over which the activation energies must be spread in order to yield the log t law over a sufficient time interval. Assuming a natural frequency of

oscillation of the domain walls of 10^9 cycles/sec., as given by Kittel(16), the range extends from 0.4 to 1.0 ev.

Jumps of domain walls over low energy barriers are associated with a decrease in dissipation factor. Using an equation by Frohlich(17), which associates this mechanism to a relaxation effect, and using the values of the observed spread in relaxation times, Plessner determined a distribution of activation energies (0.125-0.45 ev.) that completes the distribution previously indicated for the aging of the permittivity.

When the thermal transformation to the ferroelectric state occurs the domain walls may be caught in metastable positions and will require activation energies to move into stable positions. Domain walls in metastable positions requiring higher activation energies will contribute to the polarization appreciably as long as they do not surmount the high potential barrier, when they become almost inactive. The drop of power factor, accompanying the aging of the permittivity, is envisaged in terms of a domain wall being caught in an unsymmetrical potential well. The domain wall in such a state is assumed to contribute to the power factor until it passes over the higher barrier. Then, a micro-hysteresis effect for some of the domain boundaries where the restoring force for a small applied electric field is small will account for the observed power factor.

According to Plessner, the potential is of a more random nature, the more widely spaced obstacles being due to impurities, dislocations and differential strains left after the crystal structure change, and the domain walls would move in single jumps over distances which vary from a few lattice spacings to one or two microns. In his view, "Mason visualizes a potential periodic in the lattice parameter, of amplitude 19 kilo-calories per mole, and the wall moves over many periods before relieving the stress and coming to rest."

Z. Pajak(12) in a recent publication (1959) described his investigation of the aging process for Ba TiO₃-MgSnO₃ solid solutions. A new aging effect, corresponding to the displacement of the Curie point toward higher temperatures, was detected, and a new domain mechanism of aging leading to the formation of domain antiferroelectrics is proposed.

The shift in Curie point with time is explained in terms of the spontaneous relief of the mechanical stresses stored chiefly in the process of passing through the transition point to lower temperatures, when a great number of 90° domain walls accompany this initial state. Owing to the low stresses (low available energy) involved in aged samples, the Curie temperature will be higher than for young samples.

Pajak investigated also the behaviour of the dielectric hysteresis loops of young and aged samples and his results showed

that aging causes the vanishing of the spontaneous polarization (P_s). In addition, he observed the vanishing of the hysteresis losses.

Determinations of the dielectric permittivity, as a function of strong electric fields, were made by Pajak also. For young samples he found a stronger field dependence, and for aged samples he observed that the maximum of the curve shifted toward higher field strengths. These results are in good agreement with the fact that the movement of a 180° wall separating compensated domains requires more energy than the movement of a 90° wall separating non-compensating domains (18).

In general, Pajak visualizes a non-stable, highly spontaneously polarized state after cooling through the transition point, with mechanical strains stored in the sample owing to the tetragonalization of the original cubic structure, as well as to the presence of the chiefly 90° domain walls possessing domain wall energy. The large value of the depolarizing field (E_d) will favor the change in the direction of polarization in the domains. From his measurements he deduced that the spontaneous wall motion proceeds in such a direction as to reduce the spontaneous polarization and mechanical strains by causing 90° domain walls to vanish. Pajak visualizes an antiferroelectric or otherwise compensated domain arrangement so as to obtain a $P_s = 0$ for the sample as a whole. A crystal thus aged is termed a domain antiferroelectric.

A. Misarova(10) studied the dependence with time of the permittivity, loss tangent ($\tan \Delta$), and the conductivity in barium titanate single crystals. Measurements of the aging were made in the presence and absence of a constant voltage, and a lowering of the permittivity and loss tangent, not particularly different in the two cases and proportional to the logarithm of the time, was observed. The conductivity always decreased during the aging in the absence of a constant electric field; in the presence of a field it decreased up to a certain minimum and then increased.

The nature of the aging process is explained in terms of the effect of lattice defects and impurities in the crystal. Upon cooling below the Curie point, there arises a domain structure corresponding to the instantaneous distribution of defects when going through the Curie point. This is followed by a gradual localization of lattice defects and impurities at locations where they have a minimum potential energy and this, in turn, is associated with the distribution of domain walls. Existing charges in the fastened domain walls are supposed to be neutralized and as a result the mechanical stress in their vicinity is reduced to a minimum. Some regions of the crystal are considered to lose completely the ability to orientate spontaneously or under the influence of an alternating field. In other regions it is believed that the ability to orientate is worsened in one or both of the directions of the alternating field.

The observed increase in conductivity with time, at constant voltage, is not attributed to relocalization of defects but to a different process, namely, degradation. This may be thought of as intrinsic changes in the nature of the material which may account for the breakdown under the field of two of the crystals investigated by Misarova after a certain aging time.

R. Gerson(19) has investigated the aging of the voltage-dependence effect on unpolarized lead zirconate titanate and on low-aging niobium and lanthanum modifications. He determined that the effect of the measuring a.c. field on the dielectric constant and dielectric loss factor was an increase of both parameters with a corresponding increase in voltage, the higher values of the dielectric constant and dielectric loss corresponding to the modified ceramic. The behaviour of plain aged and young samples were compared also and higher values corresponding to the young samples were determined.

A hypothesis is given to explain his experimental results, which indicates that both observations are compatible with a relatively high domain wall mobility in response to the applied electric field. The high wall mobility of the modified ceramics is believed to be due to the presence of lead vacancies in the crystal lattice caused by the substitutions, which are supposed to minimize the stresses facilitating a considerable increase of domain wall mobility.

L. Kholodenko(20) explored mathematically the possibilities of a domainless, nonhomogeneous spontaneous polarization for ferroelectrics near the Curie point. The different molecular mechanisms of ferroelectricity and ferromagnetism, and the existence of an electric current having no ferromagnetic analog are pointed by Kholodenko. In view of this, he makes an attempt to break with the traditional approach which emphasizes the analogies between the ferroelectric and ferromagnetic states. He starts by assuming that a space charge with a density distribution is present and defines the spontaneous displacement distribution for the state of thermal equilibrium. With the aid of a relation for the free energy density of a single crystal with BaTiO_3 symmetry, but characterized by a phase transition of the second kind in the ferroelectric transition, he develops an expression for the depolarizing field in a domainless structure, which vanishes at the surface.

D. Dielectrics(21)

a. Dielectric constant

The dielectric behaviour of solids shows much individuality. According to Bottcher ((22), p. 422), "it is strongly dependent on the type of lattice, the degree of molecular freedom, and the chemical structure." The quantitative theory of electric polarization of solids is only in the initial stages. No completely satisfactory theory on molecular rotation is now available and a

generally accepted theory on the internal field in solids is still lacking.

The polarization of an originally uncharged dielectric is due basically to a relative displacement of positive charges in the direction of the electric field (E) and negative charges in the opposite direction. Actually the polarization may be electronic, atomic or interfacial for the case of a heterogenous material. The displaced charges, equal and opposite in sign, constitute an electric dipole. Polarization may be also due to the presence of permanent dipoles, as in the case of ferroelectric materials, which will become preferentially oriented by an external field. For all the cases the polarization vector (P) is a measure of the dipole moment per unit volume and as such must be considered as a source of an electrostatic field.

The electrical property of a dielectric, that is usually measured in the laboratory, is the absolute dielectric constant or permittivity (ϵ). The relative permittivity or dielectric constant is conveniently defined as

$$(4) \quad \epsilon_r = K = \epsilon / \epsilon_0$$

where ϵ_0 is the permittivity of vacuum and ϵ the permittivity of the material. The dielectric constant may depend on the temperature, pressure, humidity, and on the frequency of the applied electric field.

The relation between the electric field vector(E), the electric displacement vector (D), and the polarization vector (P) is given by

$$(5) \quad D = P + \epsilon_0 E \text{ coulombs/sq.ms.}$$

The electric field vector E is a measure of the local field due to all charges whether they be "free" or bound charges due to polarization of the dielectric. The electric displacement vector is a measure of only the "free charges", while P is a measure of polarization charges only.

For many gases, liquids, and solids the vectors E , P , D , have the same direction, which is interpreted to mean that the charge displacement in the dielectric has the direction of the applied field. For this particular case

$$(6) \quad D = \epsilon E \text{ and } \epsilon \text{ is a scalar.}$$

This equation can be expressed in component form along three mutually perpendicular axis (X_1, X_2, X_3):

$$(7) \quad D_1 = \epsilon E_1$$

$$D_2 = \epsilon E_2$$

$$D_3 = \epsilon E_3$$

where each component of D is proportional to the corresponding component of E . In the case of anisotropic media the previous relations will no longer hold (23) since in general ϵ will be different along different directions. Each component of D is now linearly related to all three components of E and the original

relations are replaced by

$$(8) \quad \begin{aligned} D_1 &= \epsilon_{11}E_1 + \epsilon_{12}E_2 + \epsilon_{13}E_3 \\ D_2 &= \epsilon_{21}E_1 + \epsilon_{22}E_2 + \epsilon_{23}E_3 \\ D_3 &= \epsilon_{31}E_1 + \epsilon_{32}E_2 + \epsilon_{33}E_3 \end{aligned}$$

A physical meaning can be given to each of these coefficients, assuming for instance, that a field is applied along X_1 . In this case

$$(9) \quad \begin{aligned} E &= E_1 \quad \text{and} \\ D_1 &= \epsilon_{11}E_1 \\ D_2 &= \epsilon_{21}E_1 \\ D_3 &= \epsilon_{31}E_1 \end{aligned}$$

Thus, there are now components of D not only along X_1 , but along the other axes as well. The direct component is given by ϵ_{11} and the two transverse components by ϵ_{21} and ϵ_{31} . The above analysis indicate that in order to specify the dielectric constant of some material we have to specify in general nine coefficients. These nine coefficients can be written as the components of a second rank tensor in three dimensions and the expression for the dielectric constant becomes

$$(10) \quad D_i = \sum_{j=1}^3 \epsilon_{ij}E_j \quad i = 1, 2, 3.$$

The number of coefficients necessary to specify the dielectric constant reduces to six because of the symmetric nature of this quantity.

b. Dielectric loss :

There is usually an observable time lag in the attainment of equilibrium between the applied field E , and the corresponding electric displacement D , or polarization P . This means that there exist a measurable phase difference between D and E so that the simple relation, $D = \epsilon E$ is not valid. According to Estermann(21) this phase difference may also be due to finite conductivity of the dielectric.

Polarization of a dielectric is a time dependent phenomenon. Estermann gives various figures, which will be quoted here. For electronic polarization due to displacement of electrons within an atom, the order of time required to attain equilibrium is about 10^{-15} seconds; for atomic polarization due to displacement of atoms within the molecules the time is of the order of 10^{-13} to 10^{-14} seconds. Orientation polarization of permanent dipoles requires time that depends on frictional resistance of the medium (10^{-6} to 10^{-10} seconds).

If a phase difference exists between E and D of value Δ , the complex number notation, customarily used in describing phase dependent electrical phenomena, can be used to describe these parameters as follows:

$$(11) \quad E = E_0 e^{j\omega t}$$

$$(12) \quad D = D_0 e^{j(\omega t - \Delta)}$$

where E_0 is the real part of E , $j = \sqrt{-1}$, and w is the angular frequency equal to $2\pi f$, where f is the frequency measured in cycles per second. The phase angle (Δ) depends on the electric field, the frequency, temperature, chemical composition, and structure of the dielectric. It is this dependence of Δ on molecular parameters, according to I. Estermann(21) that makes its measurement and study of importance to physical theory. The variations of Δ with E are only significant at very high field strengths. For low field intensities the following equations are valid:

$$D = \epsilon E \quad \text{and}$$

$$(13) \quad \epsilon = D_0/E_0 e^{-j\Delta} = D_0/E_0 (\cos \Delta - j \sin \Delta)$$

The complex dielectric constant or permittivity can be written as

$$(14) \quad \epsilon = \epsilon_{Re} - j\epsilon_{Im}$$

with the subscripts denoting the real and imaginary parts. From the previous equations it is obvious that

$$(15) \quad \epsilon_{Re} = D_0/E_0 \cos \Delta$$

$$(16) \quad \epsilon_{Im} = D_0/E_0 \sin \Delta$$

$$(17) \quad \tan \Delta = \epsilon_{Im}/\epsilon_{Re}$$

The imaginary part of the complex dielectric constant is called the loss factor. The phase angle Δ is sometimes called the loss angle, $\sin \Delta$ the power factor, and $\tan \Delta$ the loss tangent or dissipation factor.

The previous discussion considers polarization in homogeneous materials. In a heterogeneous material an additional type of polarization, interfacial polarization, arises, and it will be present in any dielectric, contributing to the permittivity of the material. Another limitation of this elementary approach is that for large electric fields and for materials which exhibit spontaneous polarization, the electric displacement and field are no longer linearly related, and higher order terms must be introduced(24).

Besides a formal macroscopic theory there also exists a physical theory of dielectrics that relates the measured values of the permittivity to atomic and molecular models, but no generally accepted theory for solid dielectrics has been developed. Most theoretical treatments of dielectric properties of solids are based on the concepts of local polarizability and local field developed more than 100 years ago by Clausius and Mosotti(25). The solid is regarded as composed of a large number of polarizable objects, and the mechanisms of polarization are generally thought of as distortion of electronic distributions of atoms or ions, motion of ions, or rotation of molecular aggregates having a permanent dipole moment. The dipole moment of each object is proportional to the electric field that results from the interaction of the externally applied field and the field resulting from the interaction of the polarizable objects with each other. One drastic simplification of

this whole picture is the assumed constancy of the dipole moments when no thermal agitation effects are considered.

The properties of a crystal are not merely the properties of a single molecule, multiplied by the number of molecules present, but the interactions between them are an essential part of the picture. From the point of view of quantum mechanics, it is not meaningful to speak of the state and behaviour of individual molecules or atoms. The only correct attitude is the global one in which the possible quantum states or wave functions of the crystal as a whole are enumerated.

EXPERIMENTAL PROCEDURE

A. Materials and Equipment

All the measurements made in this investigation were obtained from small ceramic disks, provided with fired-on silver electrodes obtained by Dr. R. Gerson (advisor to this work) from the Electronic Research Division, Clevite Corporation, Cleveland, Ohio.

The composition and physical dimensions of the specimens, corresponding to the quaternary system (Sr-Pb)(Ti-Zr) O₃, are the following:

Composition No.	Composition	Aver. Diam.	Aver. Thickness
1	(Pb _{0.94} Sr _{0.06})(Ti _{0.49} Zr _{0.51})O ₃	1.655 cms	1.84 mms
2	(Pb _{0.94} Sr _{0.06})(Ti _{0.48} Zr _{0.52})O ₃	1.633 cms	1.80 mms
3	(Pb _{0.94} Sr _{0.06})(Ti _{0.47} Zr _{0.53})O ₃	1.653 cms	1.85 mms
4	(Pb _{0.94} Sr _{0.06})(Ti _{0.46} Zr _{0.54})O ₃	1.644 cms	1.95 mms

To extend the working range of the bridge mica capacitors of low dissipation were used; the dissipation factor of these mica capacitors varied from (4.07-8.05)10⁻⁴ for frequencies of 1 mc. and 1 kc, respectively.

Equipment:

- a. Schering Capacitance Bridge (GR Type 716 -C)
- b. Tuned Amplifier and Null Detector
- c. Frequency Oscillator

- d. Standard Signal Generator
- e. Vacuum-Tube Voltmeter
- f. Electronic Counter
- g. Precision Capacitor
- h. Potentiometer
- i. Electric Multiple Unit Furnace
- j. Air blower, thermometer, hygroscope

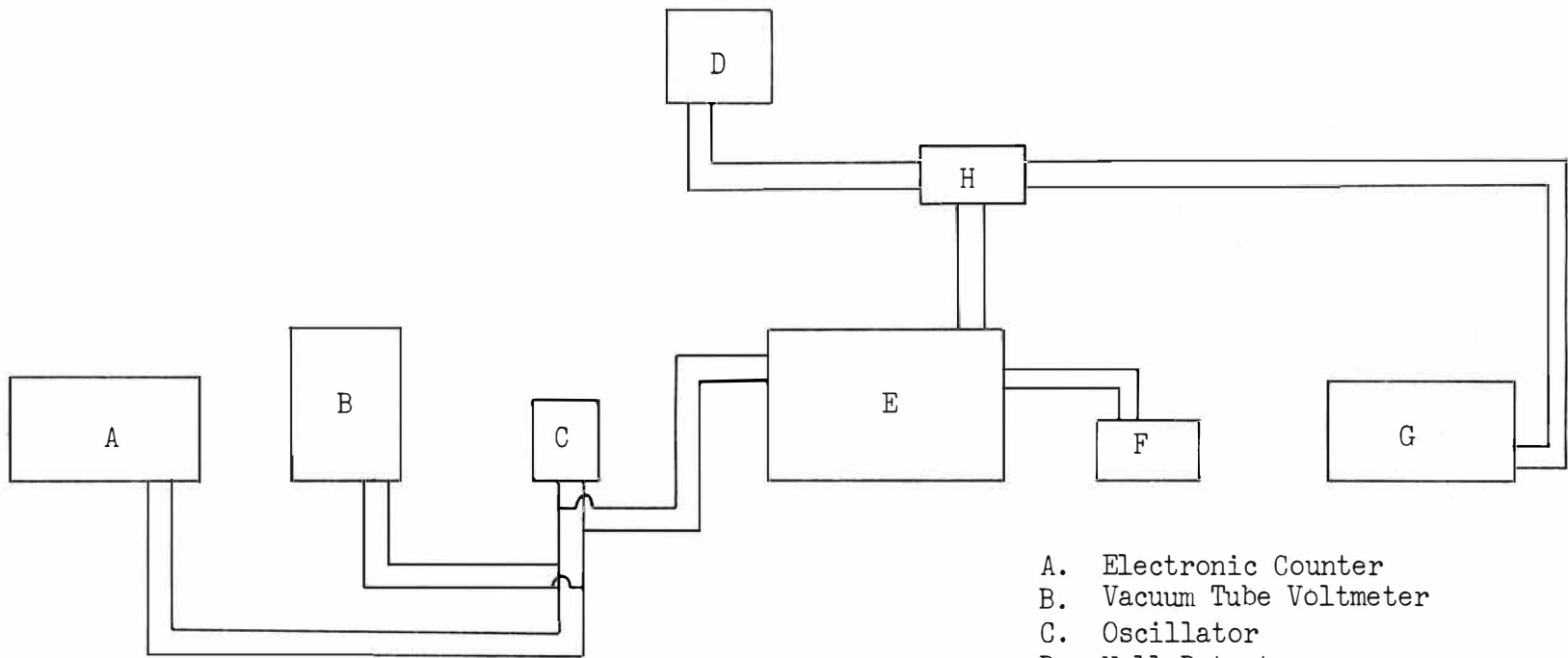
For block diagram of apparatus refer to Figure 2.

B. Measurements on Preaged Samples:

The possibility of the skin effect in the electrodes of the samples was investigated (Figure 3) at the highest frequency, 1 mc., at which measurements were made. No important electrode resistance was found.

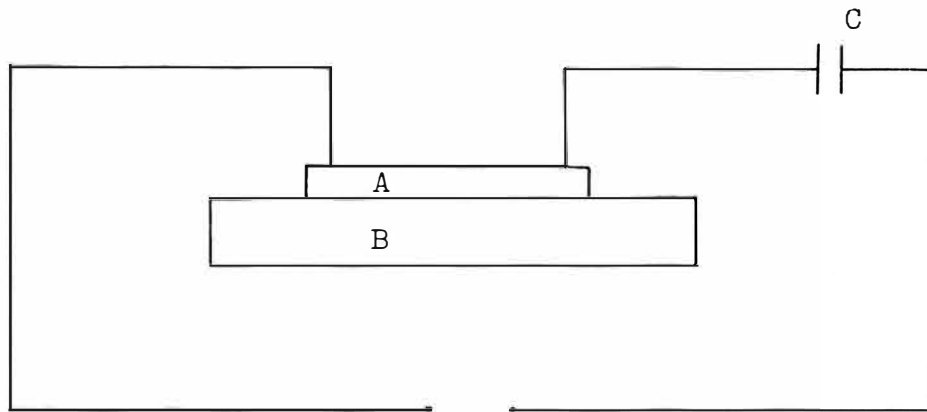
In a Schering bridge the dissipation factor measurement is made by a variable capacitor in parallel with one of the ratio arms. This control is directly calibrated in dissipation factor and the readings of the dissipation factor dial will be an indication of the energy dissipated in the bridge circuit after balancing. The introduction of an additional element in the circuit (as for example the fired on silver electrodes of the specimens investigated) will increase the dissipation of energy, if the skin effect is significant.

In the determination of the skin effect made in this investigation the readings of the dissipation factor dial with and without



- A. Electronic Counter
- B. Vacuum Tube Voltmeter
- C. Oscillator
- D. Null Detector
- E. Schering Capacitor Bridge
- F. Standard Air Capacitor
- G. Standard Signal Generator
(local oscillator)
- H. Mixer

Figure 2. Block Diagram of Equipment



- A. Ceramic Sample
- B. Plastic
- C. Capacitor

Figure 3. Skin Effect.

the additional element (sample electrode) were:

$$D \text{ (with sample)} = 0.069 \quad \text{and} \quad D \text{ (without sample)} = 0.067$$

The very small difference between the readings indicate that the influence of the skin effect was not significant.

C. Regeneration of the Aging Process

Graphs of the dielectric constant and the dissipation factor vs. frequency were determined in the fully aged samples (about 6 months aging), at room temperature, before heating to start a new aging cycle.

Determination of the transition temperatures was not necessary, since a publication by F. Kulcsar(6) places the Curie temperature of similar ceramics around 350°C. To restart the aging the four samples were heated gradually all together (with suitable identification) to 550°C and kept at that temperature for one hour. Rapid cooling to 32°C was achieved in one hour by using an air blower, the decrease in temperature being followed by using a standard potentiometer. For cooling cycle, see Figure 4.

Provision for a means to handle the samples, particularly after heating, was necessary. One of the halves of a regular size refractory brick was provided with a small cavity to hold the samples to be fired; this piece was provided also with a built-in chromel-alumel thermocouple to follow the temperature changes during the heating and cooling period (Figure 5). The other piece of refractory brick was used to cover the samples.

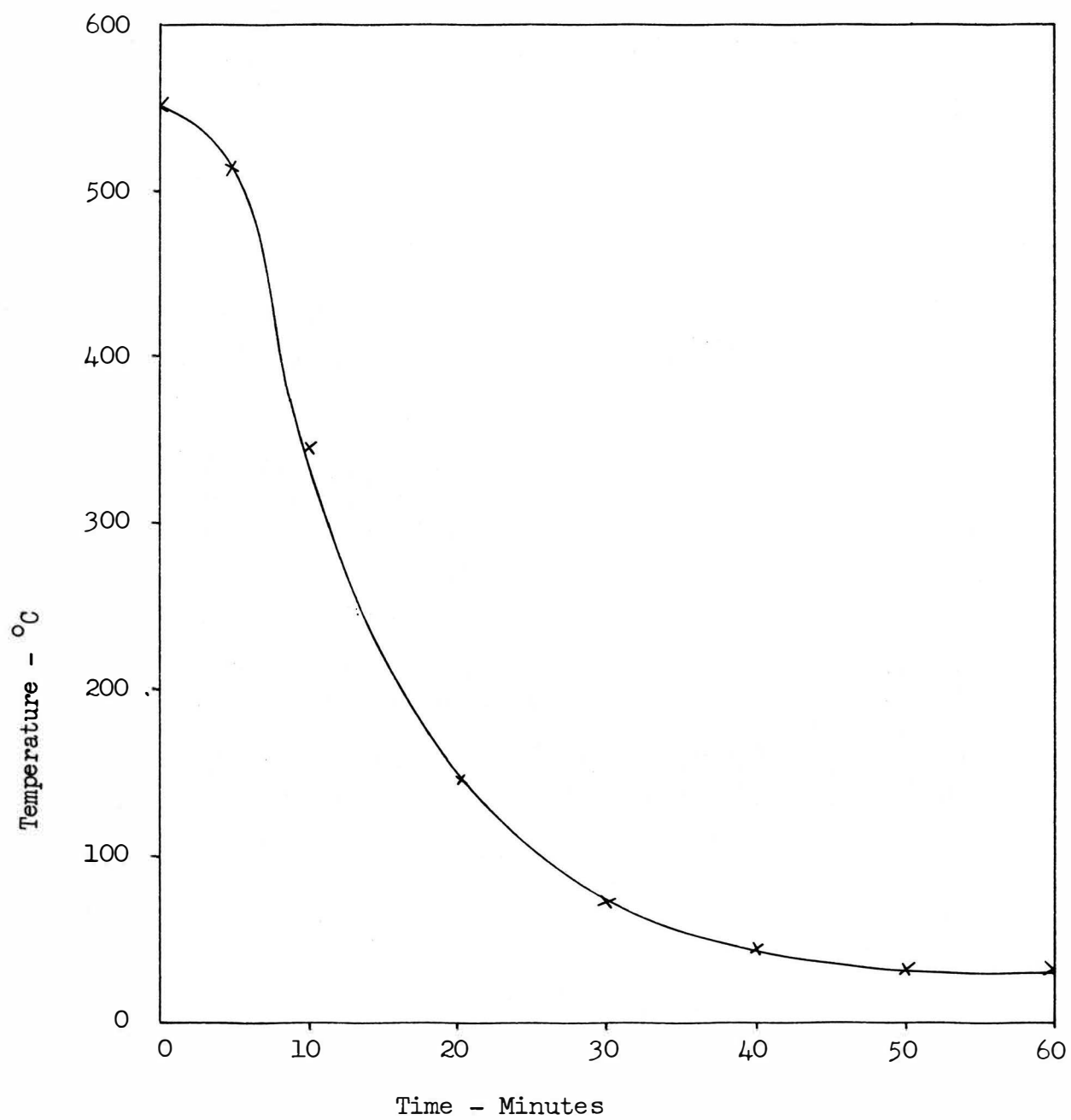


Figure 4. Cooling of Ceramics.



Figure 5. Photograph of Auxiliary Equipment.

From left to right: apparatus to keep ceramic samples at constant voltage during storage (includes transformer, resistance, and parallel plates); refractory brick pieces with built-in thermocouple; thermometer with built-in magnifying glass.

During the cooling period initial readings were taken first at five minute and then at ten minute intervals. The last reading was taken after the blower has been off for five minutes, to be sure that the sample was not very much hotter than what the potentiometer indicated.

The samples were placed at constant voltage (1 volt a.c. - 60 c.p.s.) in equipment built for that purpose previously (Figure 5). This voltage corresponds to field strengths of 5.43, 5.55, 5.41 and 5.13 volts/cm. in the order of increasing number of the samples.

Before measuring a sample its temperature was raised to $35 \pm 0.1^{\circ}\text{C}$ by using a warm stream of air (Figure 6) in two steps:

1. The sample was kept nearby the warm stream for about thirty minutes.
2. The sample was placed in the bridge (1 volt a.c., 1 kc.) directly in the main stream of warm air for about fifteen minutes (it was determined previously unaged samples attain constant temperature in about twelve minutes).

This procedure was followed mainly for the economy of time. Measurements were made early in the morning when variations in room temperature ($25\text{-}28^{\circ}\text{C}$) were relatively small. Humidity readings were taken with the recording instrument near the stream of warm air.

All readings in this investigation were made by the substitution method, using the Schering bridge type 716 -C (Figure 6). Data for



Figure 6. Photograph of Equipment.

the dielectric constant and dissipation factor measurements were taken at frequencies of 1, 10, 100, 500, and 1000 kc. For measurements at 500 kc. and 1 mc. these frequencies were beat against 600 kc. and 1.1 mc. signals from a standard signal frequency generator and then sent to a 100 kc. detector. The measuring time for all five of these frequencies in a given sample was nearly fifteen minutes in every case, which gives an average of three minutes for the reading of the data at each of the frequencies investigated. This is particularly important at the beginning of the aging period, when the greater aging rate makes it necessary to keep the measuring time at a minimum so that aging in the bridge is not significant.

The dielectric constant and the dissipation factor were measured with an accuracy of about 0.2% and 2.0% respectively, as calculated from the instruction manual formulas. Neglecting void, ground, and edge corrections, which will be the same for all the measurements in a given sample, the following formulas are used to calculate the dielectric constant and the dissipation factor.

a. Dielectric constant

$$(18) \quad K = 11.30 \frac{C}{A t}$$

t = thickness in cms.

A = area in sq. cms.

$C = C' - C$ = difference in $\gamma\gamma f.$ between first capacitance reading (without the sample) and second capacitance reading (with the sample) in the substitution method.

b. Dissipation factor

$$(19) \quad D_x = \frac{C'}{C} D$$

$D = D - D'$ = difference between second and first readings
of the dissipation factor dials.

D. Empirical Equations

A discussion of the empirical equations found in this investigation will be given. A plot on ordinary graph paper of the parameters measured vs. time was almost a straight line except for a relatively small portion at the beginning of the aging cycle. When the data was plotted on semi-log paper linearity was achieved (Figures 7-14); this suggests (26) that the data can be fitted to an equation of the form

$$(20) \quad 10^y = Rx^{-S}$$

where R and S are appropriate constants. This equation will apply except for very small and very large values of x. Taking logarithms on both sides we get

$$y = \log R - S \log x$$

which can be put in the form

$$(21) \quad y = r - S \log x, \quad \text{with } r \text{ a new constant.}$$

It is obvious that a plot in semilog paper of $\log x$ vs. y results in a straight line. In this work x will stand for the time; y will represent the dielectric constant or the dissipation factor, with r and S constants to be determined.

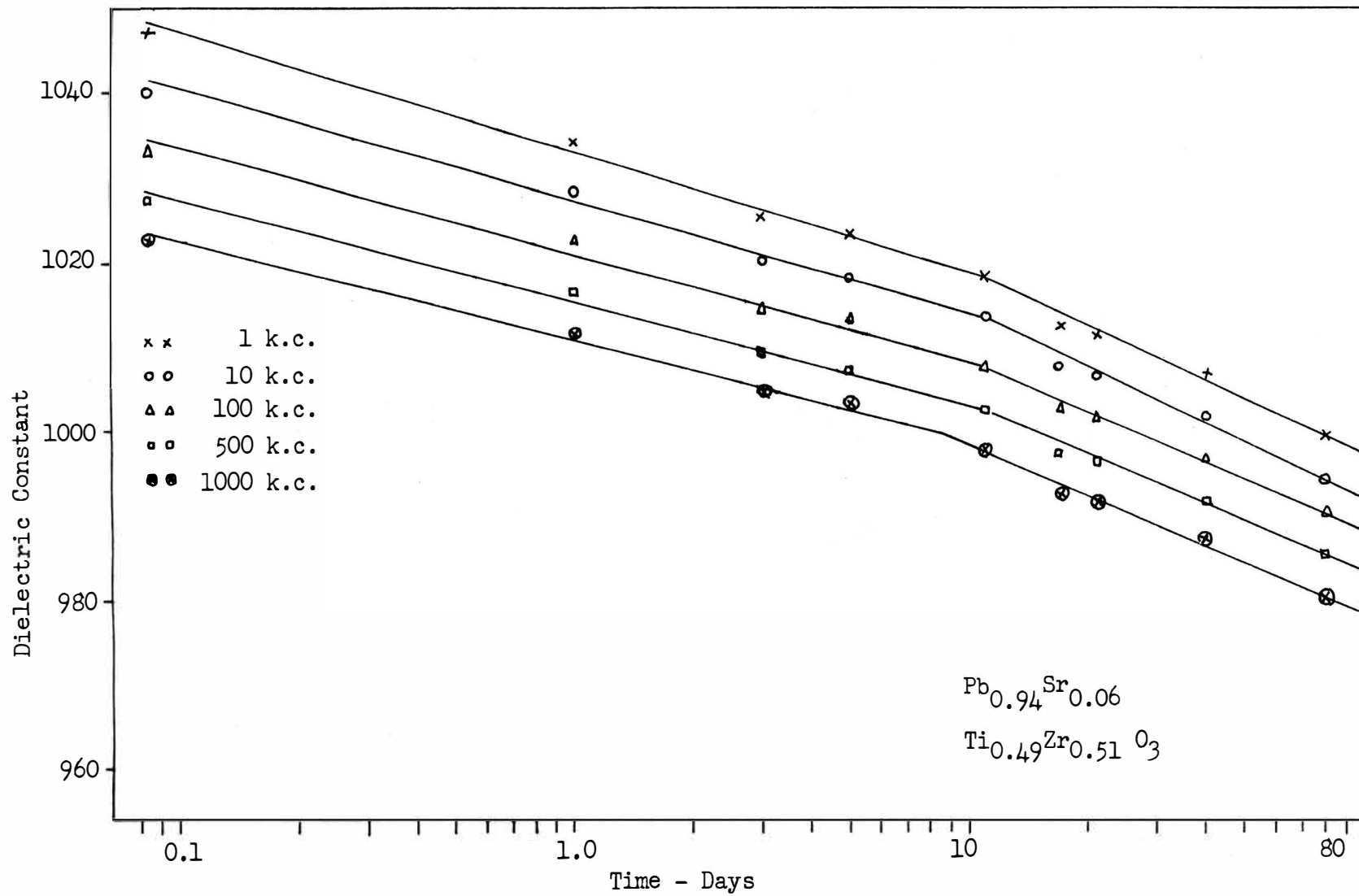


Figure 7. Aging of Ceramic Composition No. 1.

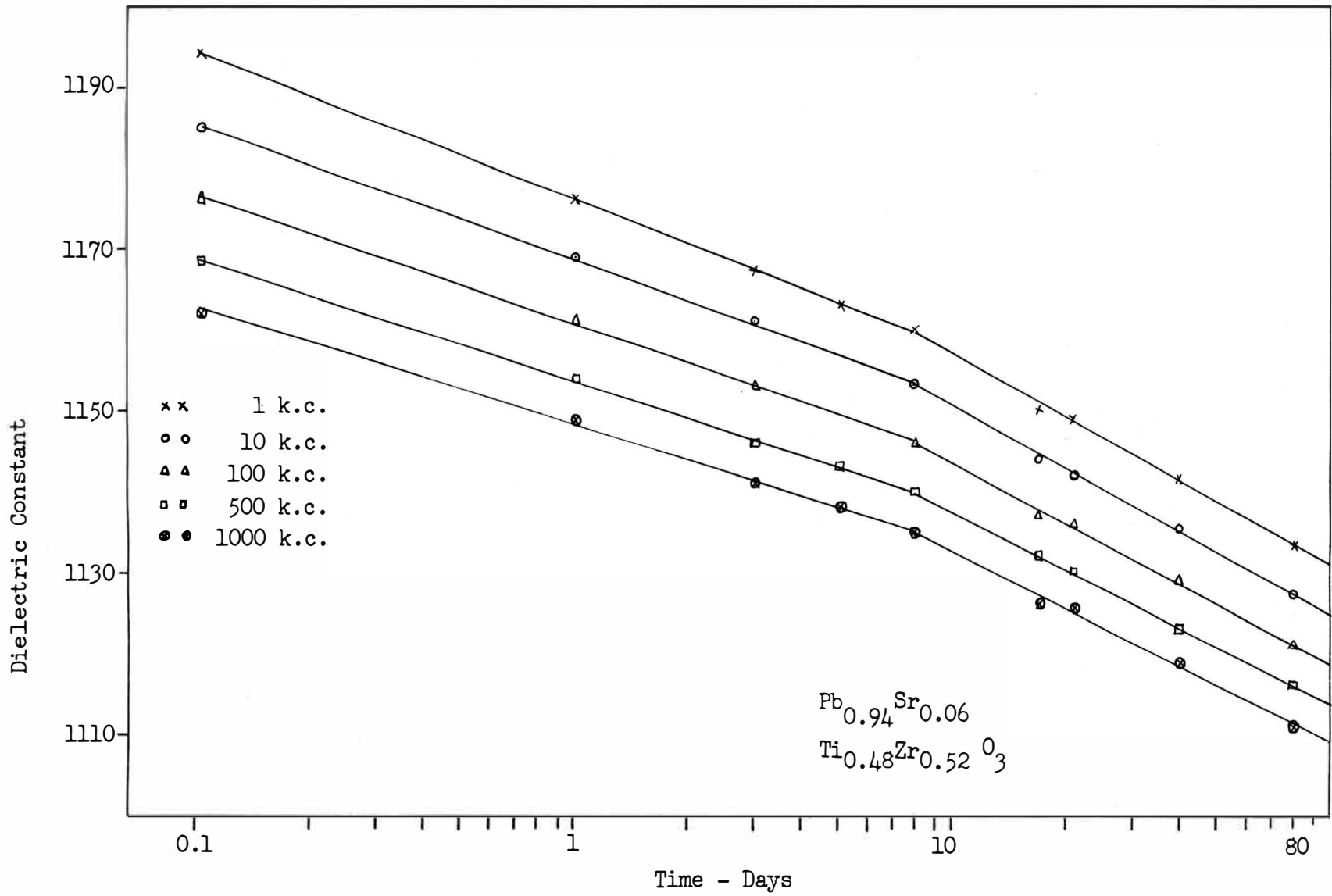


Figure 8. Aging of Ceramic Composition No. 2

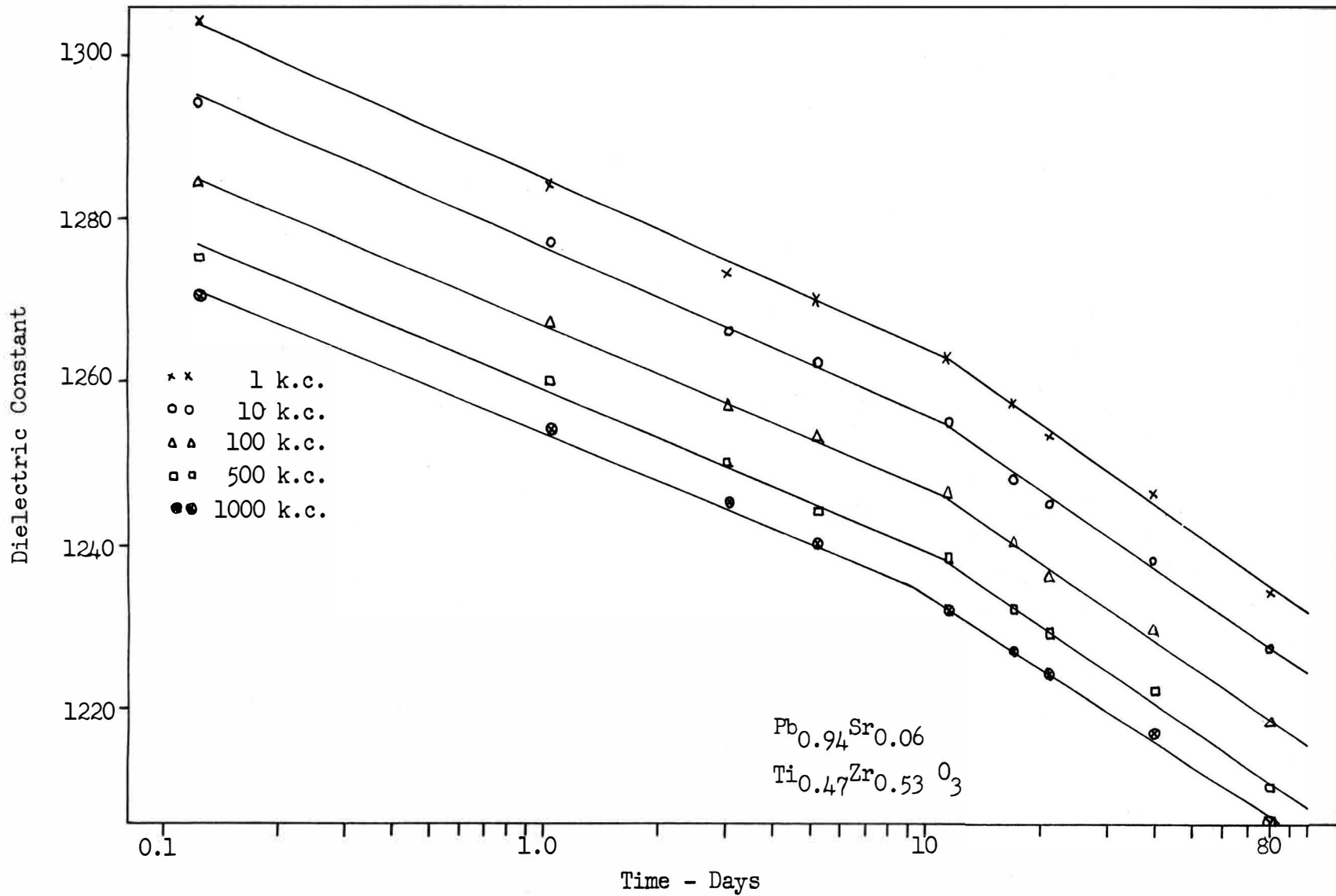


Figure 9. Aging of Ceramic Composition No. 3.

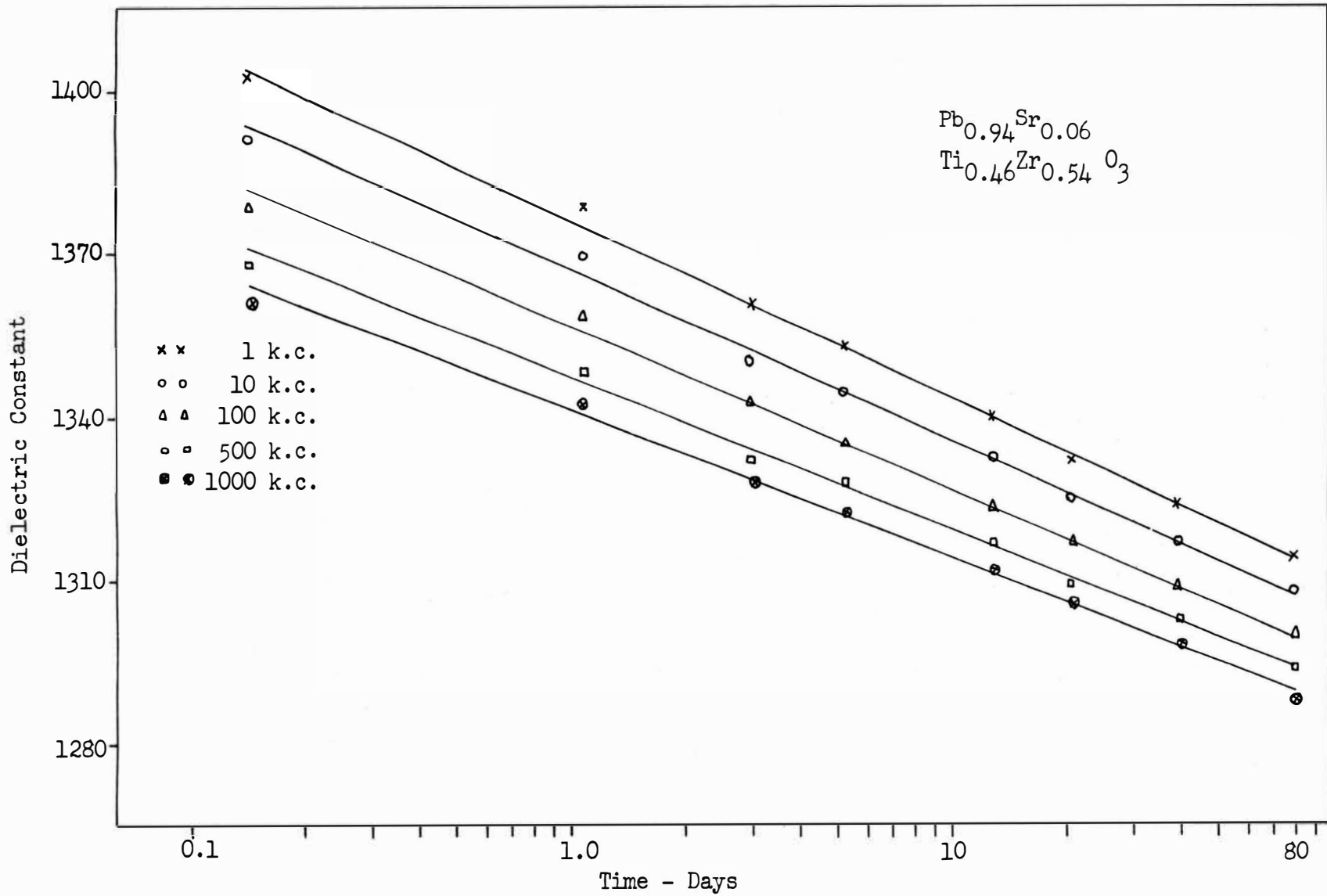


Figure 10. Aging of Ceramic Composition No. 4.

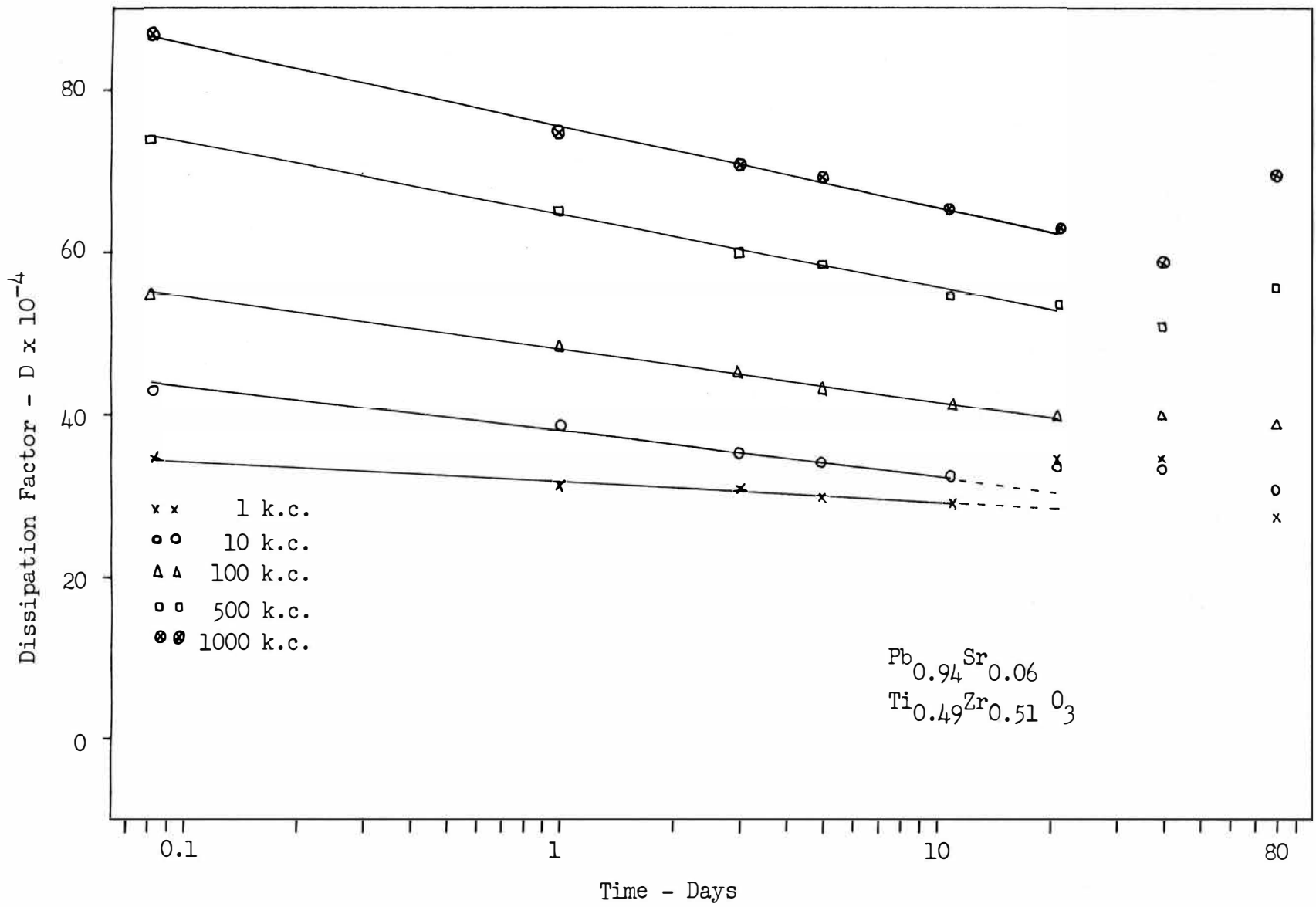


Figure 11. Aging of Ceramic Composition No. 1.

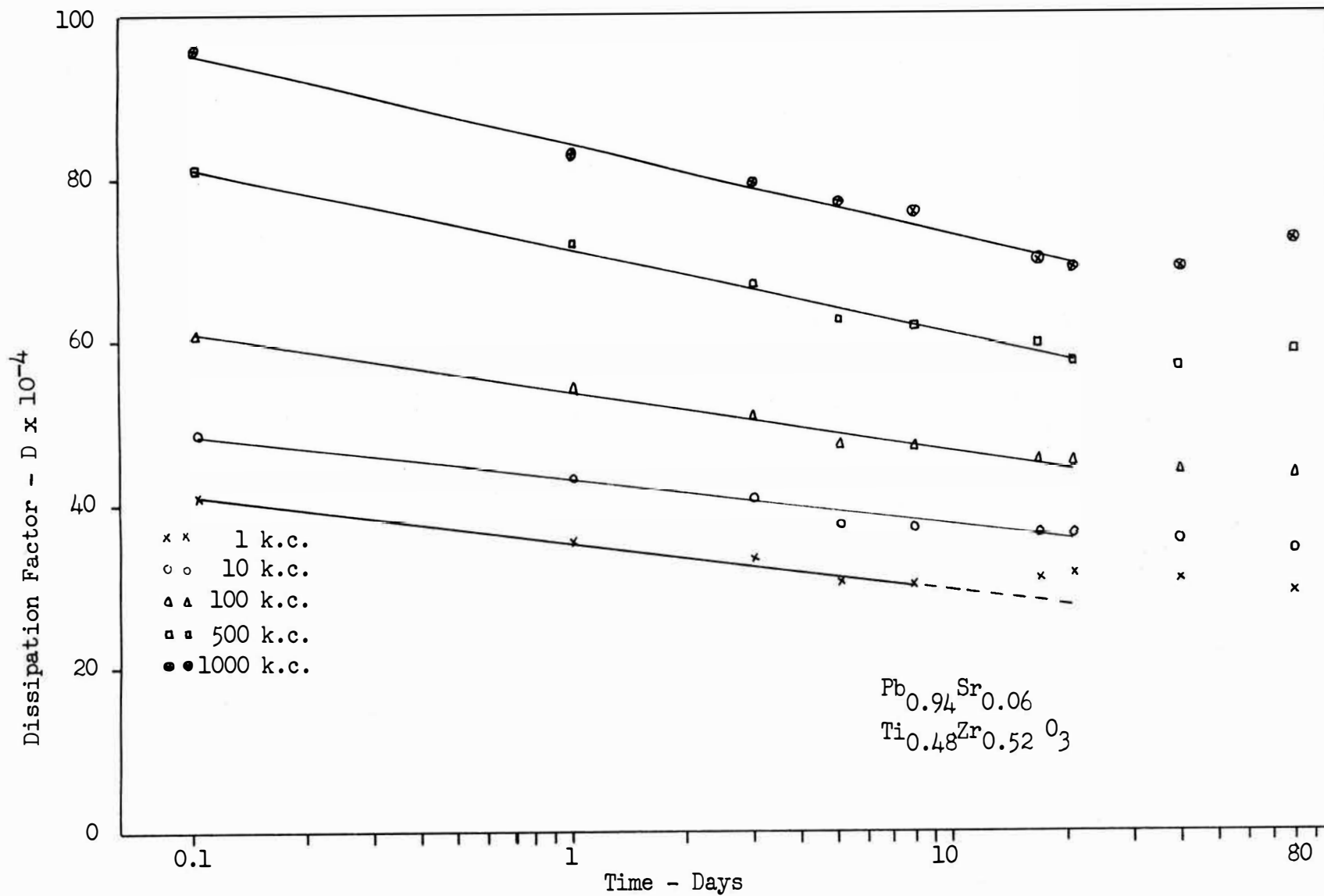


Figure 12. Aging of Ceramic Composition No. 2.

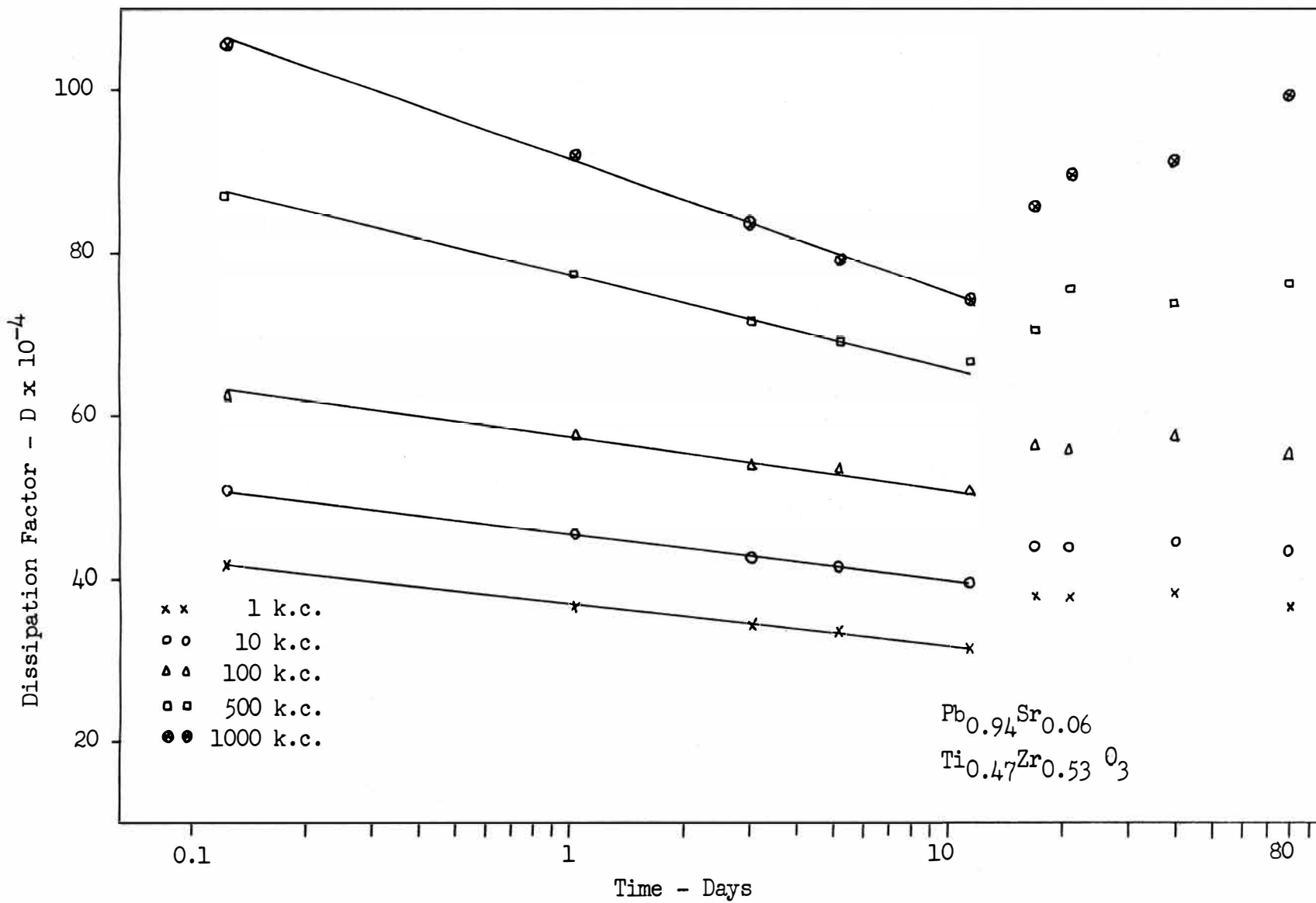


Figure 13. Aging of Ceramic Composition No. 3.

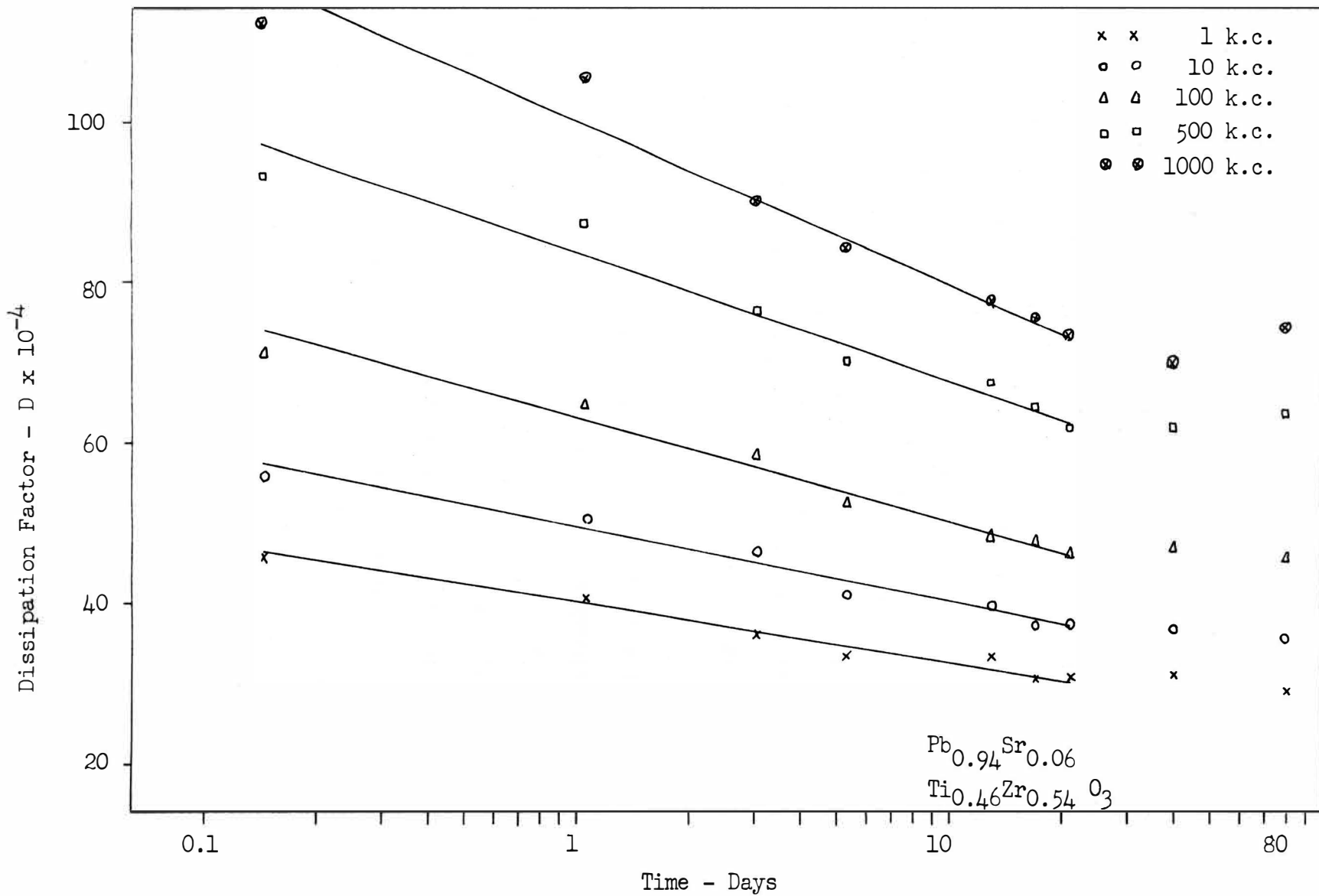


Figure 14. Aging of Ceramic Composition No. 4.

To determine the magnitude of the appropriate constants the best straight line was drawn through the data points, and the coordinates of two points near the extremities of the line were substituted in the general equation

$$y = r - S \log x$$

after which r and S were found by simultaneous solution of the two equations that result. The above procedure was applied to every sample at every particular frequency at which measurements were made. For each sample, and for every one of the two physical properties investigated, this results in five different equations, one for each frequency. The next step was to try to collect the five equations corresponding to each sample into one, by determining, if possible, how these constants varied with the frequency. For the case of the dielectric constant the two groups of r and S values were plotted separately against the $\log f$ of the frequency, and since it resulted in a very nearly straight line, a general expression relating these constants to the frequency was determined by using the same equation as before, namely,

$$y = r - S \log x.$$

This allowed expressing the constants r and S in terms of the frequency and obtaining the group of empirical equations that follows.

Dielectric Constant:

Sample No.

$$(22) \quad 1 \quad K = (1033.4 - 6.7 \log f) + (0.82 \log f - 14.3) \log t$$

$$(23) \quad 2 \quad = (1176.8 - 8.7 \log f) + (0.85 \log f - 17.2) \log t$$

$$(24) \quad 3 \quad = (1285.8 - 9.9 \log f) + (0.62 \log f - 21.1) \log t$$

$$(25) \quad 4 \quad = (1377.3 - 11.4 \log f) + (1.37 \log f - 34.4) \log t$$

f = frequency in kc./sec.

t = time in days since removal from the oven.

The range of application of the above formulas is from 1 kc. to 1 mc. and for a period of time corresponding to ten days.

The correlation of the constants and the frequency for the case of the dissipation factor proved to be more elaborate. As before, the objective was to find a general expression of the form:

$$(26) \quad D = C - C' \log t$$

with C and C' representing general expressions in terms of the frequency for the two different groups of constants. To achieve a good degree of linearity it was found necessary to use the following modifications of the originally used formula,

$$(27) \quad 1/C = b - b' \log f \quad \text{and}$$

$$1/C' = d - d' \log f \quad \text{where the } b\text{'s and } d\text{'s are constants}$$

to be determined. Only in one case, the determination of C' for sample no. 3, the above procedure failed. Instead a more complicated relation suggested by S. Davis (26) was used for this particular case. The failure of this sample to follow an empirical pattern

similar to that of the other ceramics, may be considered a prelude to the anomalously observed in the measurements associated with it, of the dissipation factor, about ten days later.

The group of empirical equations corresponding to the dissipation factor are the following:

Dissipation Factor:

Sample No.

$$(28) \quad 1 \quad D = \left(\frac{100}{3.283 - 0.648 \log f} - \frac{100 \log t}{29.20 - 6.60 \log f} \right) 10^{-4}$$

$$(29) \quad 2 \quad = \left(\frac{100}{2.880 - 0.550 \log f} - \frac{100 \log t}{18.40 - 2.90 \log f} \right) 10^{-4}$$

$$(30) \quad 3 \quad = \left(\frac{100}{2.760 - 0.550 \log f} - \frac{(1.622 - 0.280 \log f) \log t}{0.360 - 0.105 \log f} \right) 10^{-4}$$

$$(31) \quad 4 \quad = \left(\frac{100}{2.500 - 0.490 \log f} - \frac{100 \log t}{13.25 - 2.69 \log f} \right) 10^{-4}$$

By partial differentiation, with respect to the time, of the general expressions for the dielectric constant and the dissipation factor, a set of equations is determined which gives the rate of aging of the physical properties investigated as a function of both the time and the applied frequency.

Dielectric Constant

Sample No.

$$(32) \quad 1 \quad dK/dt = (0.82 \log f - 14.3) 1/t$$

$$(33) \quad 2 \quad = (0.85 \log f - 17.2) 1/t$$

$$(34) \quad 3 \quad = (0.62 \log f - 21.1) 1/t$$

$$(35) \quad 4 \quad = (1.37 \log f - 34.4) 1/t$$

Dissipation Factor

Sample No.

$$\begin{aligned}
 (36) \quad 1 \quad dD/dt &= \frac{10^{-2}}{29.2 - 6.6 \log f} \quad 1/t \\
 (37) \quad 2 \quad &= \frac{10^{-2}}{18.4 - 2.9 \log f} \quad 1/t \\
 (38) \quad 3 \quad &= \frac{-(1.62 - 0.28 \log f)}{0.360 - 0.105 \log f} \quad 1/t \\
 (39) \quad 4 \quad &= \frac{10^{-2}}{13.25 - 2.69 \log f} \quad 1/t
 \end{aligned}$$

All the empirical relations given previously were obtained with the data corresponding to the first ten days, when the aging process was more significant. On the same grounds similar equations can be arrived at for the case of the dielectric constant, if the long time effect is considered. Due to the irregular behaviour of the dissipation factor measurements, about ten days later, no useful empirical equations can be obtained in this case for the long time effect.

DISCUSSION OF RESULTS

The general expression for the dielectric constant

$$(40) \quad K = (A - B \log f) + (C \log f - E) \log t ,$$

with A, B, C, and E appropriate constants, shows that this quantity decreases linearly both with the log of the frequency and the log of the time. In this equation $B \log f$ and $C \log f$ approaches A and E respectively as the frequency increases. The dissipation factor has been found also to decrease linearly with the log of the time but to increase with the frequency.

The equation for the decay with time of the dielectric constant is

$$(41) \quad dK/dt = (G \log f - H) 1/t,$$

where G and H are constant values different for every one of the samples. The aging rate appears to decrease linearly with the log of the frequency ($G \log f$ approaches H as f increases) and to vary inversely with the time. For the dissipation factor the aging rate increases with the frequency and has the same inverse time variation. The time dependence found in this investigation for the aging rate is similar to that reported previously by other investigators (2, 3, 10). The frequency dependence is a first contribution to the aging process, within the range of frequencies measured and for the samples investigated.

The diminution of the dielectric constant with frequency and time, as indicated by equation (40), can be explained in terms of a low domain wall motion. At high frequencies the domain walls cannot easily follow the variations of the electric field due to inertia effects. The number of domain walls participating in the reorientation process will diminish with time due to their localization at more stable and less polarizable positions.

Although it appears that the aging rate of the dissipation factor increases with the frequency, the percentage-wise aging rate of this quantity is about the same at different frequencies. This may indicate that the aging rate (percentage-wise) is independent of the number of domain walls participating in the reorientation process, which seems to be physically reasonable.

The graphs of the data corresponding to the dielectric constant and the dissipation factor measurements vs. frequency (Figures 15, 16), for fully aged and young samples, demonstrate that for any of the compositions investigated the dielectric constant diminishes in magnitude with the frequency and the dissipation factor increases with it.

A plot for samples aged three days, of the dielectric constant and the dissipation factor vs. composition (Figures 17, 18), shows, for all the frequencies investigated, that the magnitude of both quantities becomes larger as the ratio of zirconium to titanium increases (lower values of c/a). The increase with composition of the dissipation factor is greater for higher frequencies. The

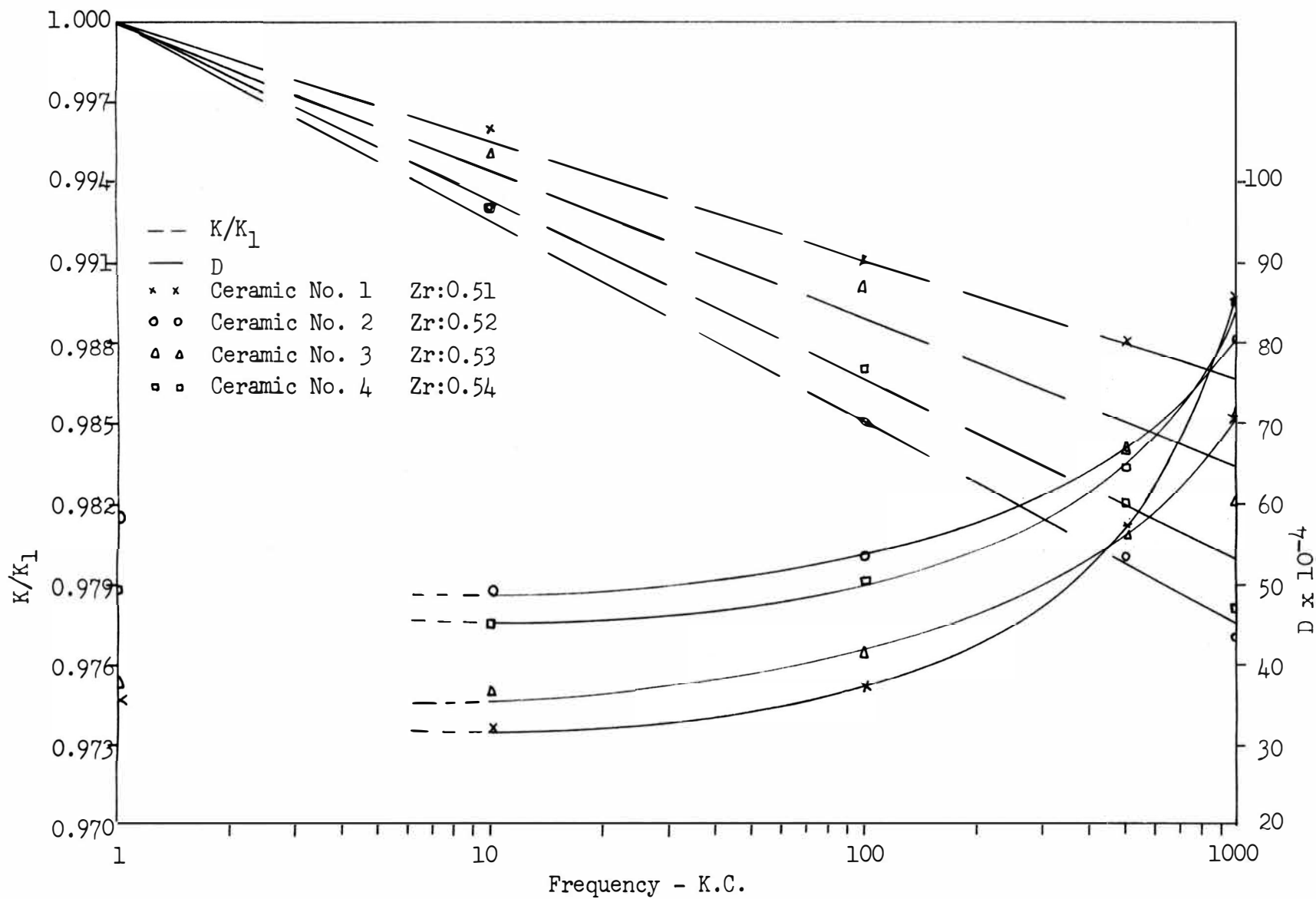


Figure 15. Dielectric Constant (K) and Dissipation Factor (D) vs. Frequency Before Heating Ceramics (Measurements at Room Temperature)

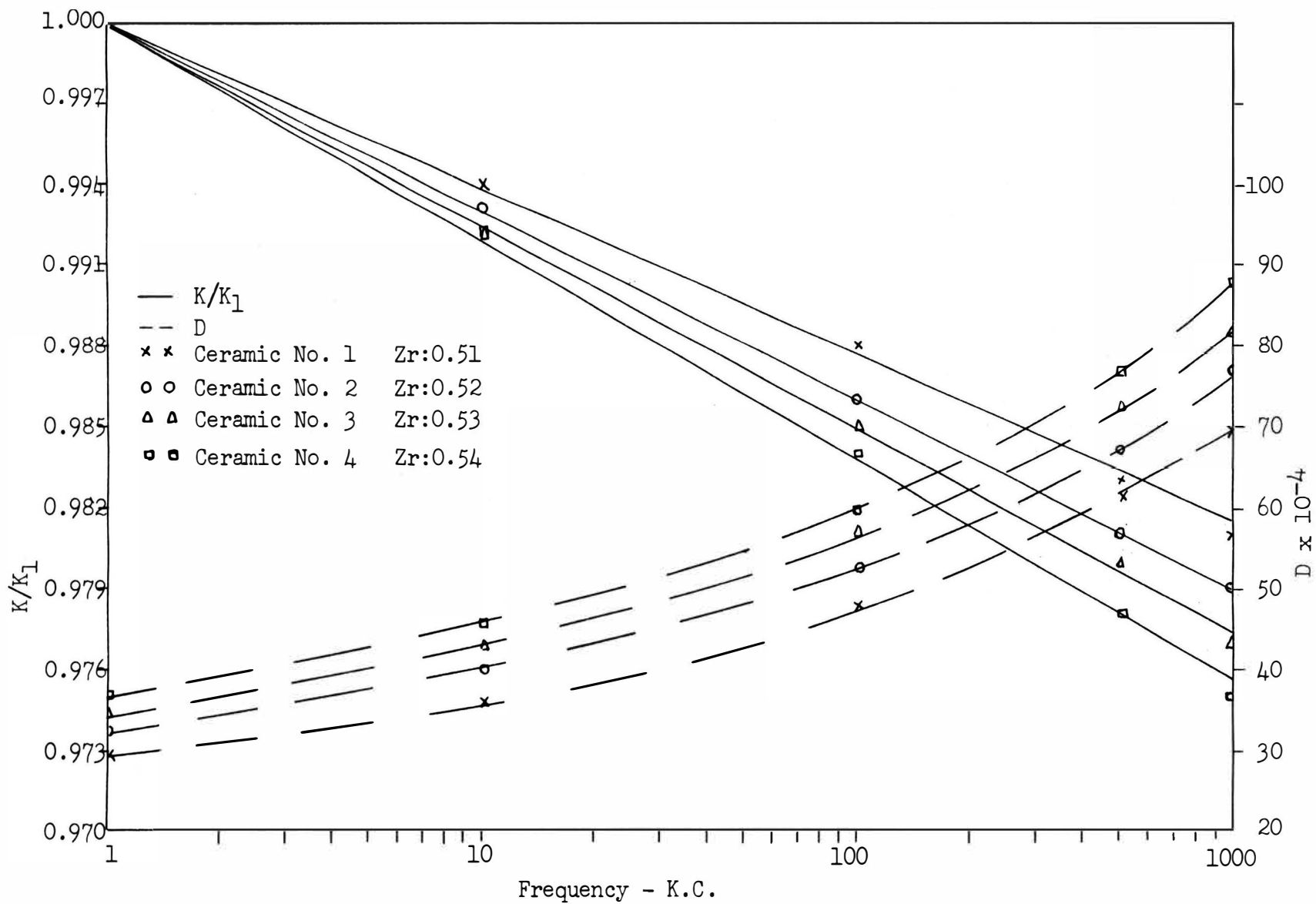


Figure 16. Dielectric Constant (K) and Dissipation Factor (D) vs. Frequency for Ceramics Aged Three Days.

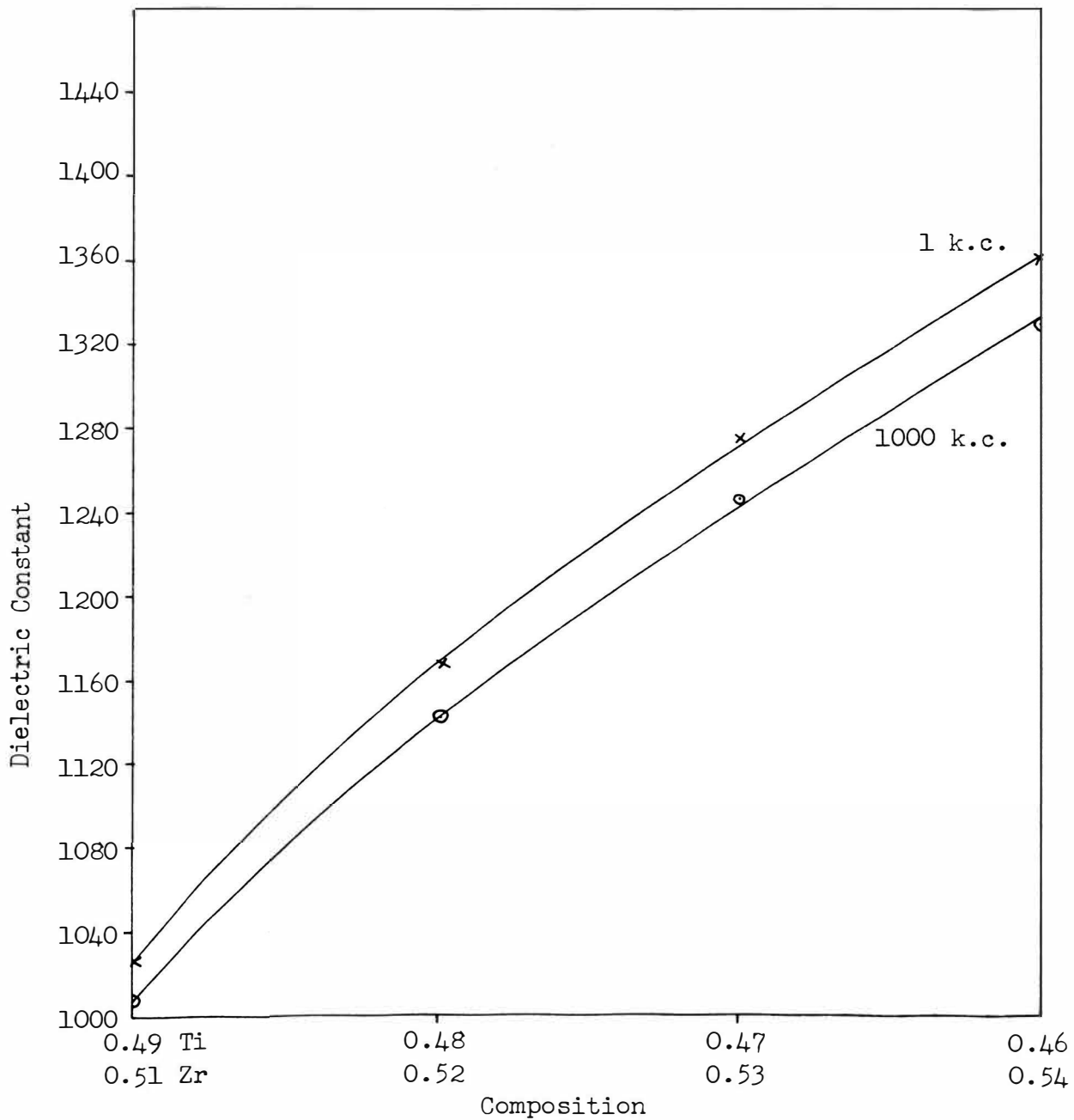


Figure 17. Dielectric Constant (K) vs. Composition for Ceramics Aged Three Days

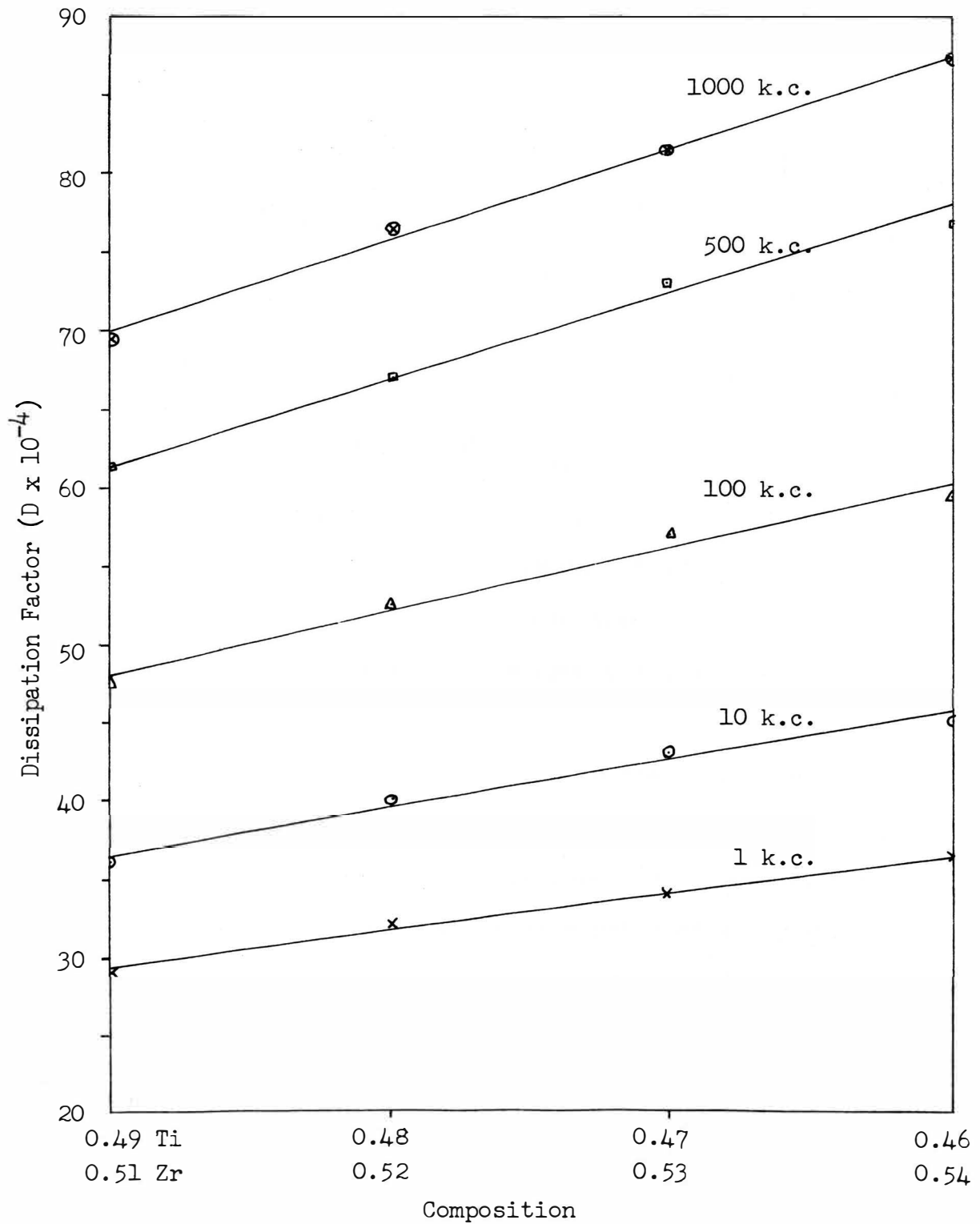


Figure 18. Dissipation Factor (D) vs. Composition for Three Days Aged Ceramics

increase of the dielectric constant with composition is less at higher frequencies. The contrary is found true for the dissipation factor. It is apparent that very small variations of the relative amounts of zirconium and titanium in these ceramics will produce significant changes in the values of the properties measured.

Two other graphs (Figures 19, 20), which collect information associated with the main purpose of this investigation, are a plot of the absolute value of the rate of change of K with time ($-dK/dt$) vs. K and also vs. the composition. Both graphs, which essentially are equal, reveal that the aging rate of K increases gradually first and then more rapidly as the boundary between tetragonal and rhombohedral on the tetragonal side is approached, or as the c/a ratio decreases. This behaviour is more pronounced at lower frequencies.

A very irregular behavior can be seen in the graph corresponding to a plot of the negative rate of change of the dissipation factor with time ($-dD/dt$) vs. the composition (Figure 21). However, the general tendency appears to be toward higher rates of aging with increasing amounts of zirconium (decrease in c/a ratio).

Higher values of dielectric constant, dissipation factor, and of the aging rates of these quantities are characteristic of compositions closer to the tetragonal-rhombohedral phase boundary. This suggests the domain wall mobility is enhanced near the morphotropic boundary.

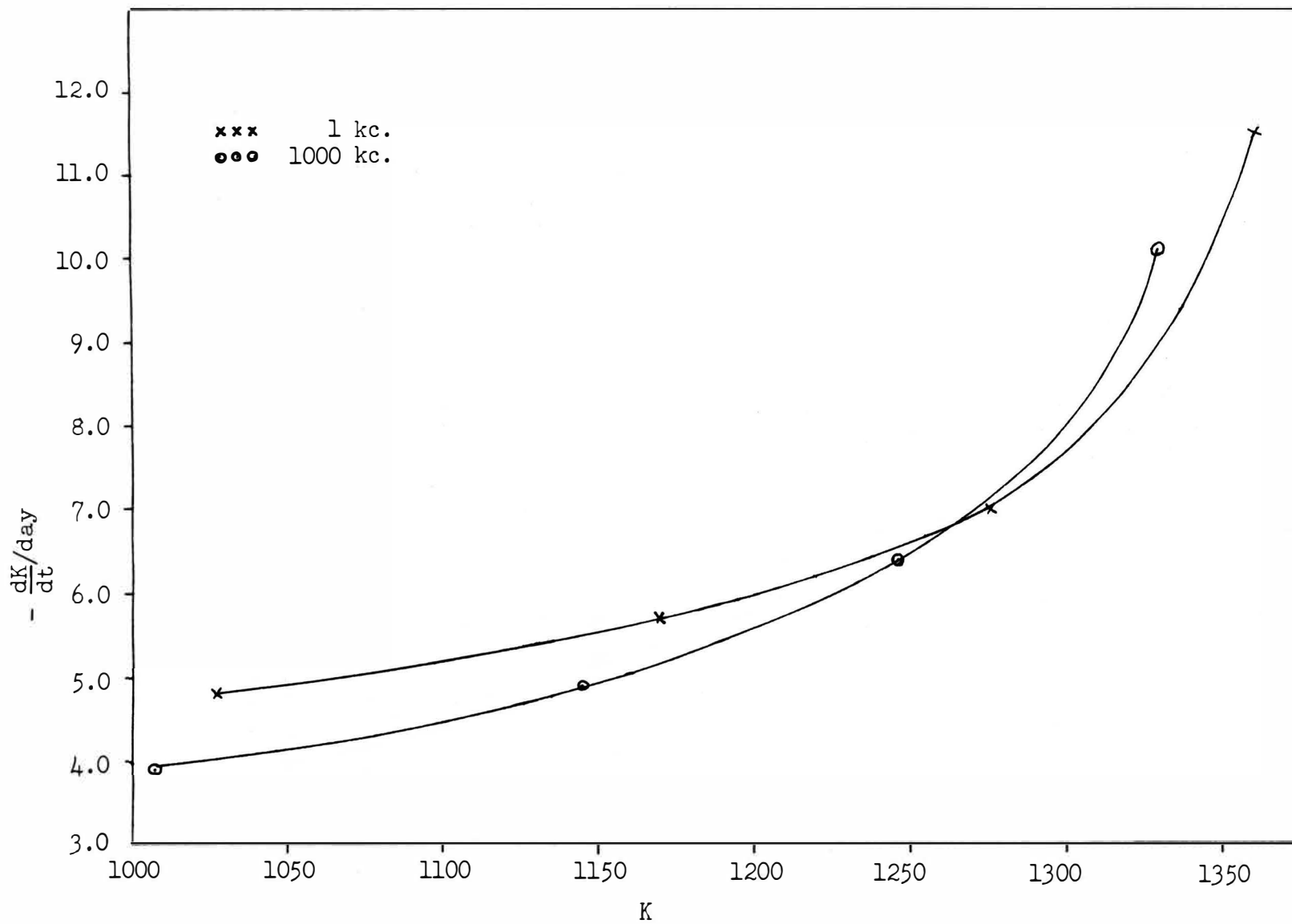


Figure 19. Rate of Aging of Dielectric Constant ($-\frac{dK}{dt}$) vs. Dielectric Constant

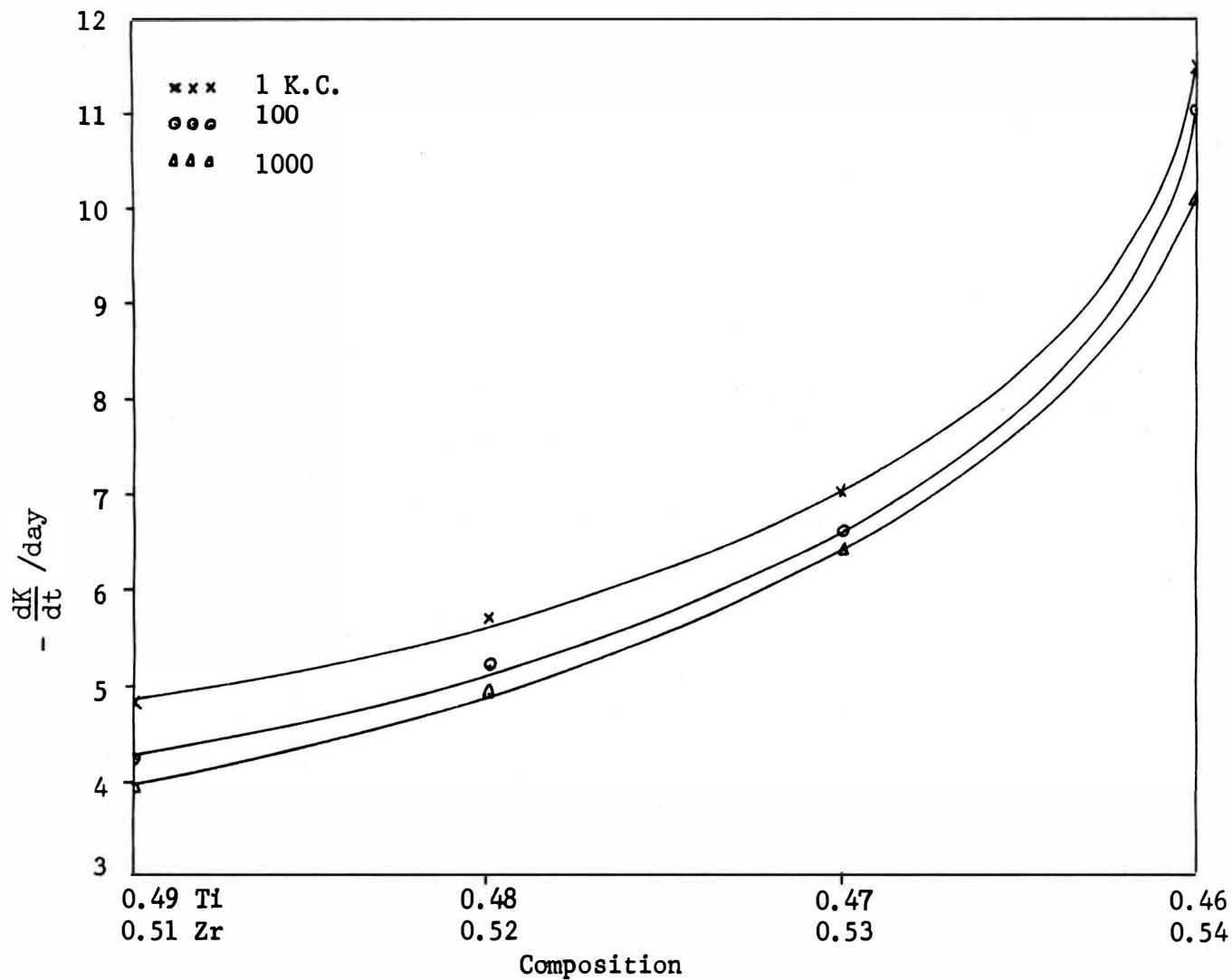


Fig. 20 Rate of Aging of Dielectric Constant vs. Composition

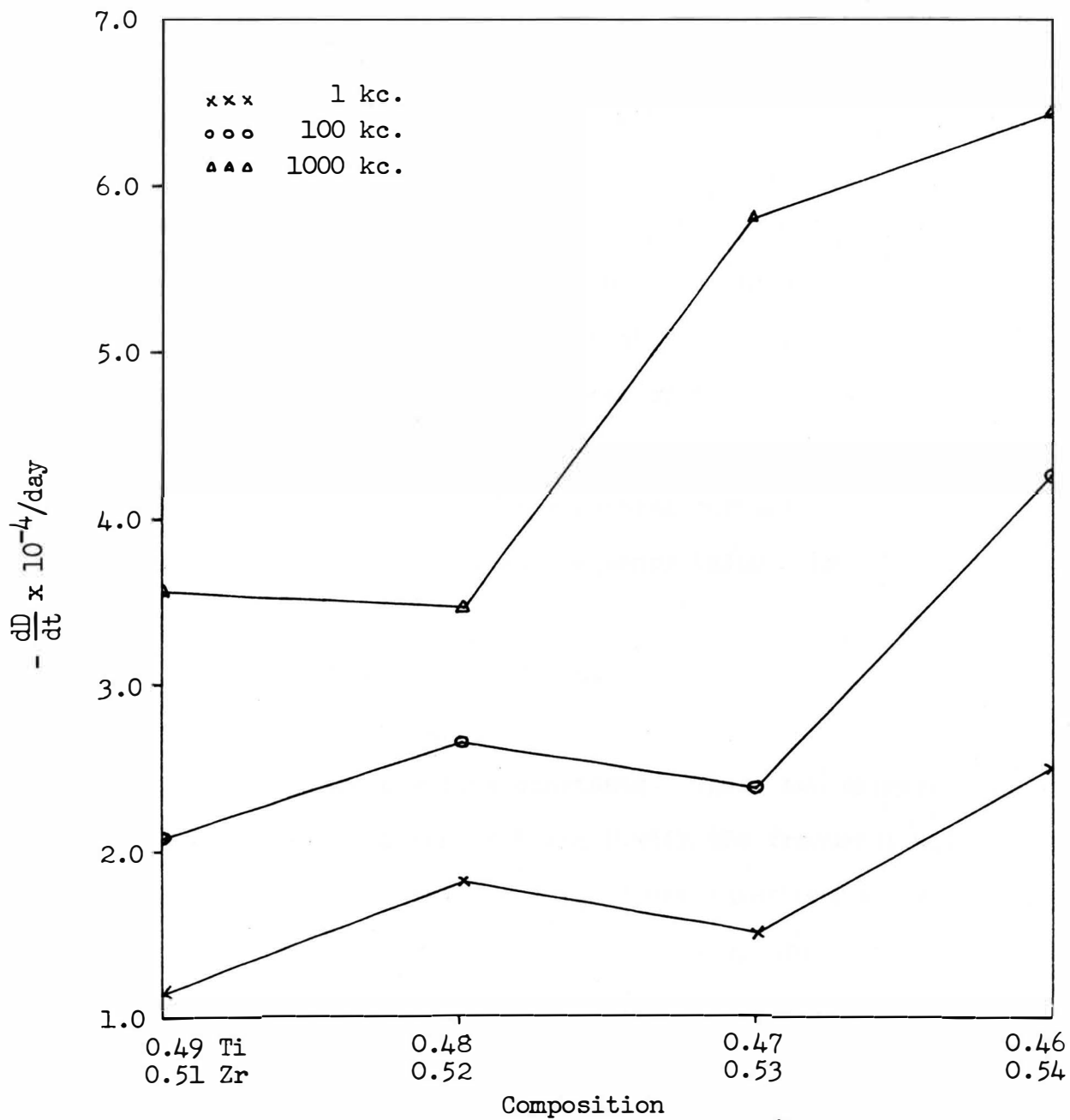


Figure 21. Rate of Aging of Dissipation Factor ($-\frac{dD}{dt}$) vs. Composition for Ceramics Aged Three Days

The most important graphical analysis (Figure 22) shows the frequency dependence of the aging rates as given by the empirical equations obtained as a result of this investigation. The plot was made for data corresponding to the third day after the aging cycle was started. The aging rates of the dielectric constant are higher at lower frequencies. The decay of the dissipation factor with time increases with the frequency. A comparison of the aging rates (percentage-wise) of both quantities measured was made at different frequencies, and it was found that the aging rate of the dissipation factor is from 8-14 times that of the dielectric constant. Refer to Table I.

A partial differentiation of the general formulas, with respect to the frequency, gives for a given frequency value the following simplified formulas:

$$(42) \quad dK/df = A \log t - B \quad \text{and}$$

$$(43) \quad dD/df = C - E \log t$$

where A, B, C, and E are positive constants. These two expressions demonstrate that the variation of K and D with the frequency will become smaller as the time increases (in these equations $A \log t$ approaches B, and $E \log t$ approaches C), which indicate that the highly polarized state which accompanies the young sample makes K and D to be more frequency dependent. The graph of $-dK/df$ vs. composition (23) shows that this quantity is greater for compositions of lower c/a ratios.

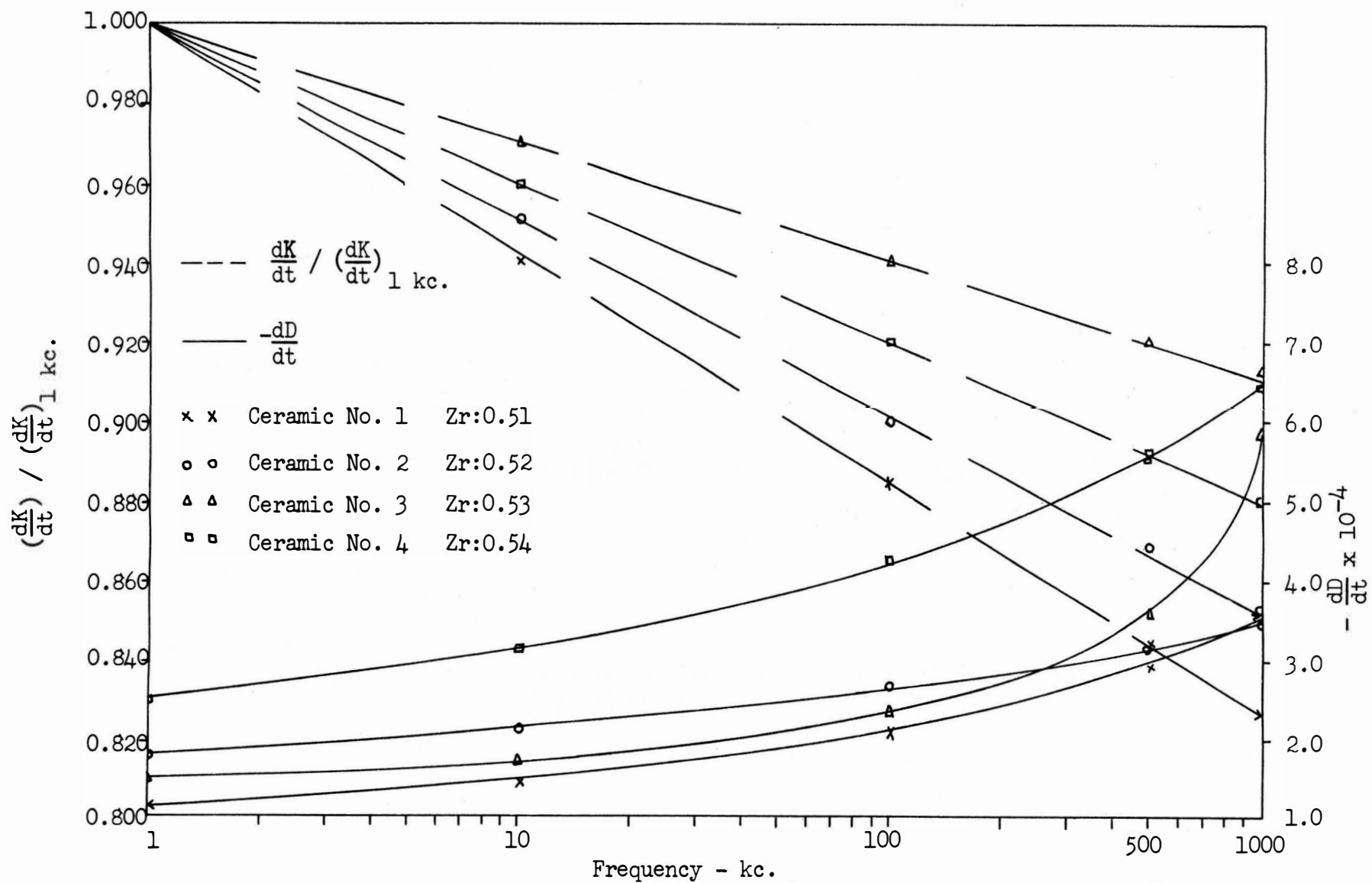


Figure 22. Rate of Aging of the Dielectric Constant ($-\frac{dK}{dt}$) and Dissipation Factor ($-\frac{dD}{dt}$) vs. Frequency for Ceramics Aged Three Days.

TABLE I CALCULATED DATA

Composition No.	Frequency (kc.)	% $(-dK/dt)l/K$	% $(-dD/dt)l/D$	$\frac{(dD/dt)l/D}{(dK/dt)l/K}$
1	1	0.47	3.94	8.4
	10	0.44	4.10	9.3
	100	0.41	4.40	10.6
	500	0.40	4.77	12.0
	1000	0.40	5.10	12.8
2	1	0.49	5.62	11.5
	10	0.46	5.40	11.6
	100	0.45	5.07	11.3
	500	0.44	4.70	11.8
	1000	0.43	4.52	11.5
3	1	0.55	4.47	8.2
	10	0.54	4.09	7.6
	100	0.52	4.15	7.9
	500	0.52	4.93	11.3
	1000	0.51	7.10	13.8
4	1	0.84	6.93	8.2
	10	0.82	6.98	8.6
	100	0.79	7.10	9.0
	500	0.77	7.24	9.4
	1000	0.76	7.33	9.6

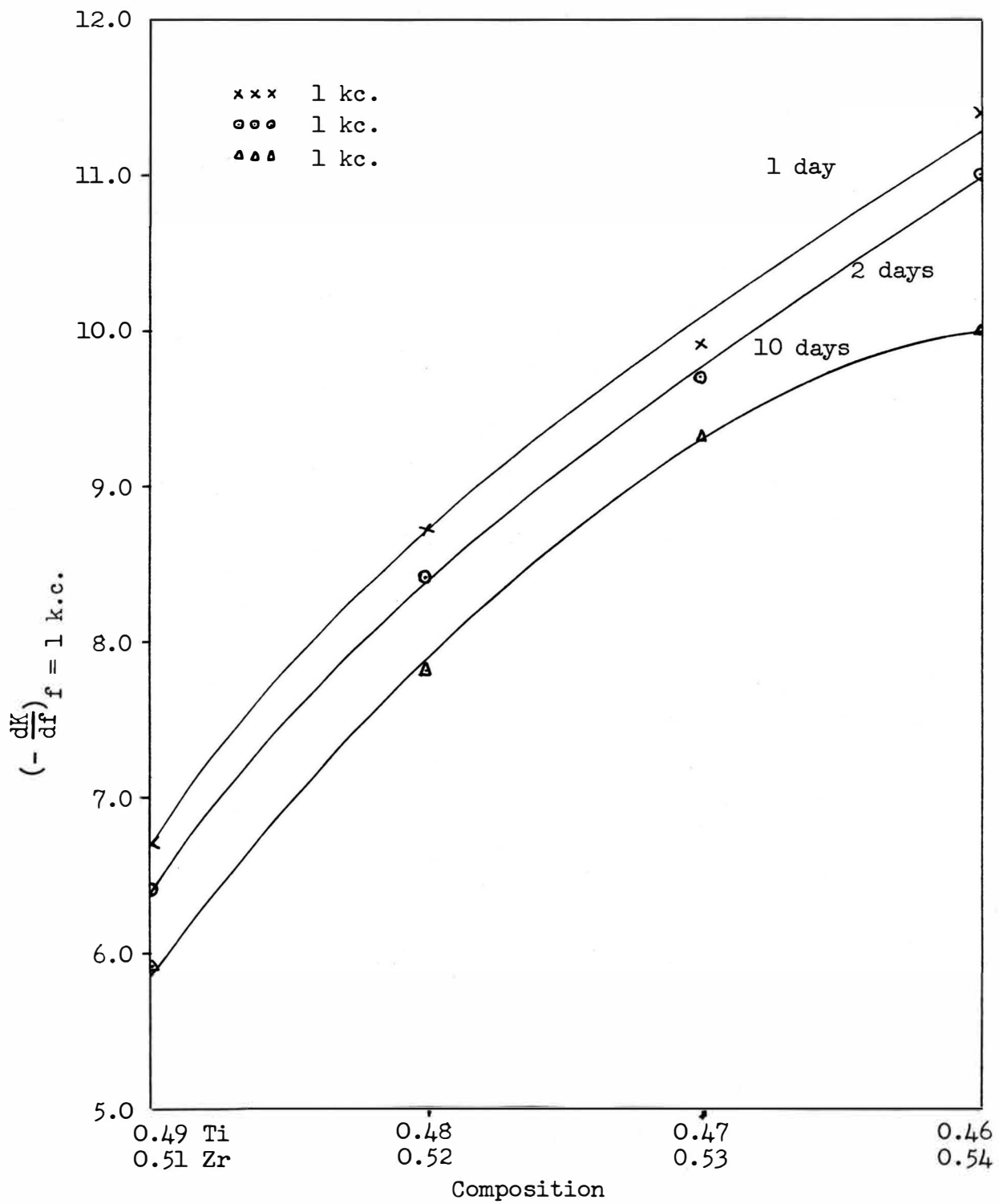


Figure 23. Variation of Dielectric Constant with Frequency $(-dK/df)$ vs. Composition.

The dissipation factor was observed to increase about ten days later after the aging process was initiated. This may be explained by an increase in the conductivity of all the samples due to humidity effects. Variations in the conductivity has been explained also in terms of a decrease in the oxygen vacancy concentration in the ceramic which it is believed may be strongly influenced by impurities(19).

SUMMARY

The rate of change of the dielectric constant with time, for a group of perovskite type ceramics, has been found to decrease linearly with the log of the frequency and to vary inversely with the time. The rate of decay (percentage-wise) of the dissipation factor is about the same for all frequencies and has the same inverse time variation.

The gradual diminution with time (aging rate) of the dielectric properties measured was found also to be altered by changes in composition, which took the samples closer to the boundary region between tetragonal and rhombohedral. The aging rate of the dielectric constant and loss factor increases for those compositions nearer to the morphotropic boundary. These were also the compositions with lower crystallographic ratios.

It is believed that under the action of an alternating electric field a large contribution is made to the dielectric constant by the motion of domain walls in the process of reorientation along the direction of the field. This motion of domain walls is lessened at higher frequencies where the domain walls cannot follow the variations of the field as easily. This results in a lowering of the dielectric constant. A gradual relocation of domain walls to more stable and less polarizable states is responsible for the observed decay with time of the dielectric constant and the dissipation factor.

The high aging rates of the dielectric constant have been found to be displaced toward low frequencies and also toward the boundary region. A physical explanation in terms of an increase of the domain wall mobility is proposed to account for these experimental observations.

High aging rates of the dielectric constant at low frequencies are due to the relatively large number of domain walls participating in the reorientation process before the attainment of more stable and less polarizable configurations.

The enhanced domain wall motion close to the boundary region is physically reasonable. It follows from the high mobility of the spontaneous polarization due to the higher number of possible polar directions in the rhombohedral state. The eight additional polarization directions along the cubic diagonal of the rhombohedral crystal-lite will add to the six possible directions of orientation of the tetragonal structure. This overall increase in the number of polarization directions will result in a larger number of domain walls participating in the reorientation process along the direction of the field. An increase of the domain wall motion will thus take place and greater values of dielectric constant and dissipation factor will be observed. These quantities will also show higher aging rates near the morphotropic boundary. This follows from a faster localization of domain walls at more stable and less polarizable positions due to the greater domain wall motion.

CONCLUSIONS

A logarithmic empirical relation was found to hold for the decay of the dielectric constant with frequency and time for a group of perovskite type ceramics with compositions close to the tetragonal-rhombohedral phase boundary. The dissipation factor increased with the frequency and decreased linearly with the log of the time.

Variations of the dielectric constant and dissipation factor with the frequency are more significant at the beginning of the aging cycle.

A hypothesis which postulates a high domain wall mobility at low frequencies or near the boundary region, is consistent with the experimental results.

Dissipation factor measurements should yield more consistent results in a completely dry atmosphere.

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VITA

The author was born on May 11, 1928 at Cabo Rojo, Puerto Rico to Antonio and Petra M. Troche. In Cabo Rojo he received his primary and secondary education. He entered the College of Agriculture and Mechanic Arts (University of Puerto Rico) in the summer of 1946. From this institution he received, in December 1950, the degree of B.S. in Chemical Engineering and was also commissioned as Second Lieutenant in the Reserve Officers Training Corps. Following his graduation he spent a short tour of active duty at the Panama Canal Zone. During the years of 1951-55 he was employed as a laboratory technician and later as an Assistant Superintendent in various sugar cane factories.

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