from the amplitude of the square wave to obtain the variation of potential across the dielectric. The change in field in the oxide was then estimated in the following manner. It was assumed that approximately 100 volts across a thickness of 10^{-4} cm provided a field of 10^6 volts per centimeter, with smaller fields corresponding to smaller differences in potential. The collector current (j_c) was measured at the beginning of the pulse, and the rise time t was measured directly. These experimental rise times were then computed and compared with the theoretical values found from Eq. (9). As shown in Table III, good agreement was found. Furthermore, it can be seen from Table III that the time lags for similar primary avalanche and self-sustained emission currents were also in good agreement.

It should be noted that there was some difficulty in estimating the area of the emitting region, and therefore the current densities may be off by a factor of three. However the order of magnitude between calculated and experimental values is close. Furthermore it can be seen that where the current density decreased, the rise time increased as predicted by Eq. (9).

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Phase Transitions in Antiferroelectric PbHfO$_3$†

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Phase transitions in ceramic PbHfO$_3$ have been studied by dielectric and structural measurements. The dielectric constant is about 90 at room temperature, and its temperature dependence shows a small anomaly at 163°C and a pronounced peak of 540 at 215°C. The *P-E* relation, however, is almost linear, showing no ferroelectric hysteresis loops within this temperature range. At room temperature PbHfO$_3$ has a tetragonal lattice of the perovskite type with $a=4.136$A and $c/a=0.991$, and a powder x-ray photograph shows some superstructure lines which have essentially the same character as those of PbZrO$_3$. This shows that PbHfO$_3$ is an antiferroelectric of the PbZrO$_3$ type below 163°C. The crystal structure between 163°C and 215°C is also based on a tetragonal lattice; but the axial ratio c/a is much closer to unity (0.997), and the observed superstructure lines are different from those of the lowest phase. Thus the intermediate phase is another antiferroelectric phase, with a different type of dipole arrangement from that of the lowest phase. At 215°C, it becomes paraelectric, accompanied by a change to a cubic structure.

I. INTRODUCTION

RECENT studies of PbTiO$_3$ [1,2] and PbZrO [3,4] have revealed interesting dielectric properties and relations of these to the crystal structures of these perovskite-type compounds. PbTiO$_3$ is a ferroelectric with a Curie point of 490°C,[2,5] and this is very similar to the much studied Curie point of BaTiO$_3$ [6] at 120°C. The crystal structure[7] of PbTiO$_3$ is distorted to a tetragonal lattice with $c/a=1.063$ below its Curie point. The dielectric properties of PbZrO$_3$, on the other hand, have shown that this crystal is not ferroelectric but antiferroelectric with a Curie point at 230°C, notwithstanding the close resemblance of the permittivity *vs* temperature curve of this crystal to those of BaTiO$_3$ and PbTiO$_3$. The crystal structure[7] of PbZrO$_3$ is distorted to a tetragonal cell, but the axial ratio c/a is less than unity (0.99), in contrast with BaTiO$_3$ and PbTiO$_3$ in which c/a is greater than unity.

No satisfactory explanation has been given of the reason why such an essential difference in dielectric and structural properties can be observed in these very closely related perovskite crystals. Although there is no doubt that the large polarizability of the Pb ion in both compounds contributes to these peculiar phenomena, the essential difference in the compounds is in the ionic radii and polarizabilities of B ions in the ABO$_3$ type crystals which have Pb as a common *A* ion. This fact suggests that the further study of lead compounds with different *B* ions, such as PbHfO$_3$, may give more information about this phenomenon.

Compared with a detailed study of titanates and zirconates of perovskite-type crystals, very little information is available on the properties of hafnates.

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[1] G. H. Jonker and J. H. van Santen, Chem. Weekblad **43**, 672 (1947).

[2] G. Shirane and S. Hoshino, J. Phys. Soc. Japan **6**, 265 (1951).

[3] Sawaguchi, Shirane, and Takagi, J. Phys. Soc. Japan **6**, 333 (1951).

[4] Shirane, Sawaguchi, and Takagi, Phys. Rev. **84**, 476 (1951).

[5] H. H. Rogers, Technical Report 56, Laboratory for Insulation Research, Massachusetts Institute of Technology, 1952 (unpublished).

[6] See A. von Hippel, Revs. Modern Phys. **22**, 221 (1950).

[7] H. D. Megaw, Proc. Phys. Soc. (London) **58**, 133 (1946).

The crystal structure of $SrHfO_3$ [8] and $BaHfO_3$ [9] has been reported as a cubic perovskite type, and the lattice constants are shown in Table I, in which comparison is made with the results on $SrZrO_3$ and $BaZrO_3$.[7] It is noticed here that hafnates have smaller lattice constants than those of the corresponding zirconates. This is due to the fact that Hf^{+4} ion has a slightly smaller ionic radius, 0.84A, compared with 0.87A for Zr^{+4}, because of the lanthanide contraction.[10] Since no measurements on $PbHfO_3$ appear to have been published, a detailed study was made of the dielectric and structural properties of this crystal.

II. CRYSTAL STRUCTURE AT ROOM TEMPERATURE

Ceramic $PbHfO_3$ was prepared from $PbCO_3$ and HfO_2. One gram of HfO_2 was obtained from the Fairmount Chemical Company, with a stated purity of 99.5 percent, with 0.3 percent ZrO_2, and 0.2 percent TiO_2. Rough estimation by spectrographic examination, carried out by Professor R. Hayes of the Department of Chemistry, The Pennsylvania State College, indicated the existence of Zr in an amount from 0.03 to 0.3 percent. Equimolar proportion of this HfO_2 and reagent-grade $PbCO_3$ were mixed well, pressed into a pellet, and fired at about 1200°C after preliminary firing at about 1000°C.

A difficulty in preparing $PbHfO_3$ ceramic arises from the high volatility of PbO during firing. A similar difficulty was encountered in the case of $PbTiO_3$ [5] and also (more pronounced) with $PbZrO_3$. But in $PbHfO_3$ the evaporation is so severe that, using the ordinary firing process, the surface of the sintered specimen changes from tan to white and a powder x-ray photograph of the surface material shows some weak lines due to HfO_2. The small supply of HfO_2 did not permit development of a completely satisfactory method for prevention of the evaporation, but the following procedure was tried.

A pressed pellet was placed between two platinum sheets to retard the evaporation of PbO during firing. The firing was carried out rather quickly, by heating to 1200°C in 4 hours and cooling down in 6 hours. The specimen thus obtained was a homogeneous and hard ceramic, tan in color. This specimen was used for the dielectric and structural studies. As shown below, it shows well-resolved diffraction lines in the powder photograph. No chemical analysis was carried out of the final specimen.

Powder photographs of this ceramic were taken with a Norelco powder camera (11.4 cm diameter), using CuKα radiation. Diffraction lines clearly show line splittings due to a distorted perovskite structure, and all multiplets can be well explained by assuming a tetragonal cell with c/a less than 1. The lattice constant and axial ratio calculated from (510), (431), and (422) line groups are $a=4.136(\pm 0.001)$A and $c/a=0.991(\pm 0.001)$. The comparison of these lattice parameters with those[7] of $PbTiO_3$ and $PbZrO_3$ are shown in Table II. As expected from the difference in ionic radii of Hf and Zr, $PbHfO_3$ shows a slightly smaller unit cell volume than that of $PbZrO_3$.

TABLE I. Lattice constants of alkaline earth zirconates and hafnates.

$SrZrO_3$	4.101A	$SrHfO_3$	4.069A
$BaZrO_3$	4.189A	$BaHfO_3$	4.173A

It is to be noted here that the c/a ratio for $PbHfO_3$ is less than unity, as in $PbZrO_3$. Moreover, some extra lines can be observed in the $PbHfO_3$ powder photograph besides the main lines due to a perovskite structure. Careful comparison of these extra lines with those of $PbZrO_3$ shows that both have essentially the same character not only in spacing but also in relative intensities. These facts strongly suggest that $PbHfO_3$ has the same type of superstructure as $PbZrO_3$, which was studied by Sawaguchi *et al.*,[11] using a single crystal method. It should be noticed here that this superstructure of $PbZrO_3$ is due to an antiparallel displacement of Pb ions in the $[110]$ and $[\bar{1}\bar{1}0]$ directions; therefore, the true symmetry is probably orthorhombic.

Beside the very close resemblance between the x-ray powder patterns of these two compounds, we can find a large difference in the ratio of the intensity of odd $N=h^2+k^2+l^2$ to that for even N. This can be explained well by the difference in the atomic scattering factors of Zr and Hf.

TABLE II. Lattice parameters of lead compounds at room temperature. $\lambda=1.5405$A was used as the Cu $K\alpha_1$ wavelength.

Crystal	a axis (A)	c/a	Unit cell volume $(A)^3$
$PbTiO_3$	3.905	1.063	63.30
$PbZrO_3$	4.159	0.988	71.06
$PbHfO_3$	4.136	0.991	70.06

III. DIELECTRIC PROPERTIES

The specimen for dielectric measurements was a ceramic disk 1 mm in thickness and 0.3 cm^2 in area, and silver paste was applied to both surfaces as electrodes. The dielectric constant of this specimen at room temperature is about 90 at a frequency of 10 kc/sec and a field strength of about 10 v/cm. Figure 1 shows the dielectric constant as a function of temperature. Heating and cooling rates were about 1°C per minute.

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[8] S. Naray-Szabo, Müegyetemi Közlemenyek No. 1, 30 (1947). Monoclinic structure with double lattice constant is also assigned to this crystal.

[9] Private communication from H. Graenicher (1952). Recently, we measured the lattice constant of this crystal using a Norelco 11.4-cm powder camera, and obtained $a=4.172$A, in good agreement with the Graenicher's result.

[10] These values of ionic radii (Goldschmidt radii) are taken from A. F. Wells, *Structural Inorganic Chemistry* (Oxford University Press, London, 1950), p. 71.

[11] Sawaguchi, Maniwa, and Hoshino, Phys. Rev. **83**, 1078 (1951).

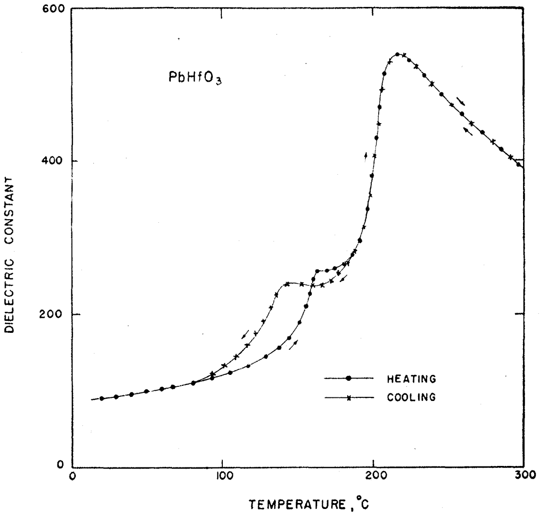

FIG. 1. Dielectric constant *vs* temperature for $PbHfO_3$, at 10 kc/sec.

This curve shows two anomalies: one is a small anomaly at 163°C, which suggests the existence of some kind of phase change; another is a pronounced peak at 215°C which can be considered a Curie point. While there is little temperature hysteresis around the Curie temperature, relatively large hysteresis is observed around the lower transition point. No anomaly was found between room temperature and -180°C.

From the crystal structure at room temperature, we can expect antiferroelectric properties of $PbZrO_3$ type in the phase below 163°C, and there is no doubt about the paraelectricity above 215°C. To study the dielectric response of the intermediate phase, we examined the relation between polarization and electric field under an ac amplitude of 30 kv/cm and 60 cycles/sec, using a Sawyer and Tower circuit.[12] The *P-E* relation is almost linear in all three phases except for a slight upward curvature just below the Curie point. A double hysteresis loop of butterfly shape, which was observed in pure $PbZrO_3$ [4] just below the Curie point (see Fig. 8 of reference 4), was not observed in this specimen up to a field strength of 40 kv/cm.

The effect of a dc biasing field of 10 kv/cm on the dielectric constant of $PbHfO_3$ was studied, with the results shown in Fig. 2. The measurements were carried out in a bath of silicone fluid, to improve the insulation as well as the temperature uniformity. In contrast with ferroelectric $BaTiO_3$, in which the dielectric constant decreases with increasing biasing field above and below the Curie temperature,[13] the slight increase of the dielectric constant was observed just below the Curie point at 215°C, and at the same time the transition temperature is decreased by 2.0°C by this field. No remarkable effect was found around the lower transition point. These results should be compared with the similar results observed in $PbZrO_3$.[4]

From this we can conclude, taking into account the crystal structure at room temperature, that the phase below 163°C is antiferroelectric, as observed in $PbZrO_3$ (phase *A*I) and that the intermediate phase is another antiferroelectric phase (*A*II) which must differ from phase *A*I in some way.

Above the Curie point the temperature dependence of the dielectric constant obeys approximately the Curie-Weiss law $\epsilon = C/(T-T_0)$, with $C = 0.95 \times 10^5$ and $T_0 = 50$°C. This value of the Curie constant is of the same order of magnitude as those of $BaTiO_3$ and $PbZrO_3$.

IV. STRUCTURAL CHANGES AROUND THE PHASE TRANSITIONS

As shown in Fig. 1, the dielectric constant *vs* temperature curve shows two anomalies at 163° and 215°C, indicating two phase changes. To study the structural changes at these two phase transitions, a series of powder photographs at various temperatures were taken, using a Unicam 19-cm diam high temperature x-ray camera. A powdered ceramic was sealed in a hard glass capillary of 0.4 mm in diameter and 0.01 mm in wall thickness. Below 163°C the diffraction patterns are essentially the same as at room temperature, except that the *c/a* ratio tends toward unity; at the same time the intensity of extra lines decreases gradually as 163°C is approached from below. Above 215°C the photographs show a cubic perovskite lattice without any superstructure lines.

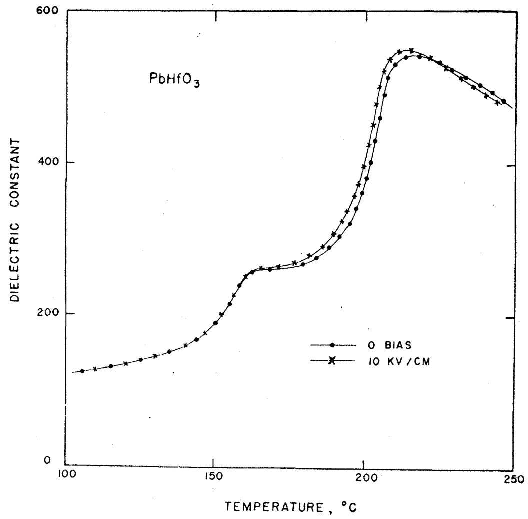

FIG. 2. Effect of dc biasing field of 10 kv/cm on the dielectric constant of $PbHfO_3$.

The diffraction pattern at 200°C, which is in the intermediate phase, is very close to a cubic pattern, and we can observe multiplets only in a few high-angle lines such as (420), (422) and (431), (530) groups. In

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[12] C. Sawyer and C. Tower, Phys. Rev. **35**, 269 (1930).

[13] S. Roberts, Phys. Rev. **71**, 890 (1947); also Cross, Dennison, Nicolson, and Widdington, Nature **163**, 635 (1949).

such a case it is difficult to determine the structure from powder photographs only. We tried to explain these multiplets by assuming simple cases such as tetragonal $c/a>1$ and $c/a<1$, orthorhombic, and rhombohedral lattices. It appeared that the multiplets could be explained if we assumed a tetragonal lattice with $c/a<1$. The lattice parameters and c/a calculated from (510), (431), and (422) lines are $a=4.134(\pm0.001)$A and $c/a=0.997(\pm0.001)$.

The dielectric test showed that the dielectric properties of this middle phase may be antiferroelectric. Careful examination of powder photographs revealed a few rather weak superstructure lines, which are different from those found at room temperature both in spacing and in relative intensity. This indicates that some kind of rearrangement of antiparallel displacement of ions does occur at the transition point of 163°C, though the both phases above and below this transition point have the tetragonal lattice with $c/a<1$. The detailed crystal structure of the intermediate phase must await a single crystal study.

The temperature change of lattice parameter calculated from the (510) (431) line group is shown in Fig. 3. Around the phase transition at 163°C, the c axis increases considerably while the a axis shows a small decrease, resulting in the volume change of about 0.15A^3. At 215°C, the structure changes to a cubic lattice accompanied by the volume increases of about 0.16A^3. To show these volume changes from another viewpoint and to compare them with the results for PbZrO$_3$, the linear region in the cubic phase was extrapolated to lower temperature and compared with the actual volume. The anomalous volume contractions in the two antiferroelectric phases are

$$-0.16\text{A}^3 \quad (\Delta v/v=-23\times10^{-4}) \quad \text{at } 200^\circ\text{C},$$

$$-0.27\text{A}^3 \quad (\Delta v/v=-39\times10^{-4}) \quad \text{at } 130^\circ\text{C}.$$

The estimated volume expansion coefficients are

$$20\times10^{-6}/^\circ\text{C below } 158^\circ\text{C},$$

$$27\times10^{-6}/^\circ\text{C above } 215^\circ\text{C}.$$

Recent studies of PbZrO$_3$ and of solid solutions derived from PbZrO$_3$ by replacing Pb or Zr ions by other suitable ions show peculiar phase diagrams. In the case of Pb(Zr-Ti)O$_3$ [14] and (Pb-Ba)ZrO$_3$,[15] the rhombohedral ferroelectric intermediate phase was observed; and, on the other hand, in the case of (Pb-Sr) ZrO$_3$ [15] the tetragonal antiferroelectric intermediate phase was found. A comparison of superstructure lines observed in the intermediate phase of (Pb$_{0.95}$Sr$_{0.05}$) ZrO$_3$ between 175° and 200°C, and those found in the intermediate phase in PbHfO$_3$ between 163° and 215°C showed that the superstructure lines seem to have essentially similar spacing and relative intensity, suggesting that they are probably the same phase, although these lines are too weak to permit definite conclusion. Moreover, the dielectric properties as shown in Figs. 1 and 2, and also the temperature dependence of lattice parameter of PbHfO$_3$, resemble very closely the corresponding results observed in (Pb$_{0.95}$Sr$_{0.05}$)ZrO$_3$.

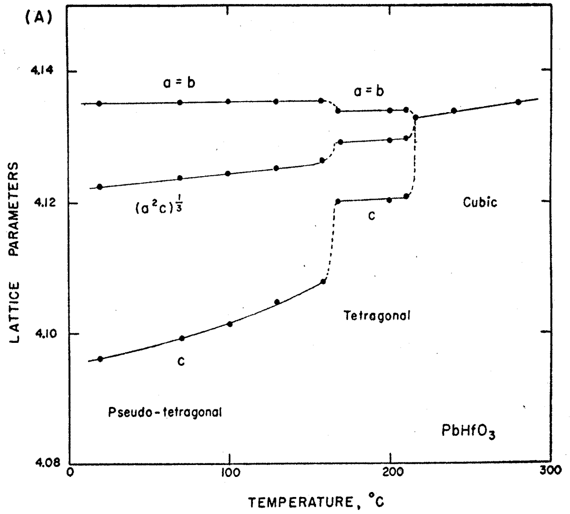

FIG. 3. Lattice spacing *vs* temperature for PbHfO$_3$.

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[14] G. Shirane and A. Takeda, J. Phys. Soc. Japan **7**, 6 (1952); also G. Shirane and K. Suzuki, J. Phys. Soc. Japan **7**, 333 (1952).

[15] G. Shirane, Phys. Rev. **86**, 219 (1952); also G. Shirane and S. Hoshino, Phys. Rev. **86**, 248 (1952); Acta Cryst. (to be published).