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X-Ray and Neutron Diffraction Study of Antiferroelectric Lead Zirconate, $PbZrO_3$†

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The room-temperature structure of antiferroelectric lead zirconate, $PbZrO_3$, has been studied by x-ray and neutron diffraction. The symmetry is orthorhombic (pseudotetragonal) with lattice parameters $a=5.88$ A, $b=11.77$ A, $c=8.22$ A. The space group is *Pba*2 and there are 8 formula units in the unit cell. The structure results from slight distortions of the cubic perovskite lattice, which the crystal assumes above 230°C.

With respect to the ideal perovskite structure, Pb atoms suffer antiparallel shifts along the former cubic [110] direction; oxygen atoms also suffer antiparallel shifts within the (001) plane and, in addition, unbalanced antiparallel shifts along the *c* direction.

The noncentric symmetry is in accord with the presence of a small piezoelectric effect as reported by Roberts. The oxygen octahedra surrounding the Zr atoms appear to be distorted, and it is possible to explain the strong optical anisotropy within the (001) plane as well as the pseudotetragonality ($b=2a$).

INTRODUCTION

DOUBLE oxides of the perovskite type have become of large interest in solid state physics in recent years.[1] These oxides have the formula ABO_3, where A is a monovalent or divalent cation, and B is correspondingly pentavalent or tetravalent. Many of these compounds are characterized by very drastic anomalies in dielectric constant at certain temperatures, which anomalies are indicative of corresponding phase transitions. Some of the transitions are called ferroelectric, since the crystals show, in the lower-temperature phase (or phases), a spontaneous electric polarization which can be reversed by an externally-applied field. The leading representatives of this class of crystals are $BaTiO_3$, $PbTiO_3$, and $KNbO_3$. Certain other transitions are called antiferroelectric, in the sense given by Kittel,[2] since dielectric anomalies appear, but no net spontaneous polarization can be observed in the lower phase, where the crystal structure is characterized by antiparallel displacements of certain atoms. The most important representatives of this class of antiferroelectric crystals are $PbZrO_3$, $NaNbO_3$, and $PbHfO_3$.

Common to these double oxides with the general formula ABO_3 is the fact that, at higher temperatures, they all have a cubic structure of the perovskite type, represented schematically in Fig. 1(a). Taking the origin at the position of the A atom, the coordinates of all the atoms are then:

$$A \text{ (Pb, Ba, K, Na, etc.) at } (0,0,0);$$
$$B \text{ (Ti, Zr, Nb, Hf, etc.) at } (\tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2});$$
$$\text{O at } (\tfrac{1}{2},\tfrac{1}{2},0),\ (\tfrac{1}{2},0,\tfrac{1}{2}),\ (0,\tfrac{1}{2},\tfrac{1}{2}).$$

This structure is often looked upon as being built by linear chains of BO_6 octahedra, extending along every ⟨100⟩ direction, and sharing all corners [Fig. 1(b)]. In lower phases these octahedra may or may not be distorted,[3,4] depending on the size and polarizability of the atoms A and B.

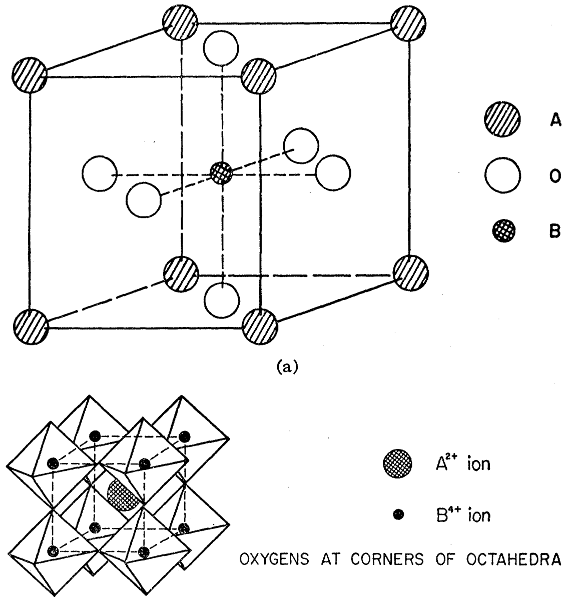

FIG. 1. (a) Cubic perovskite-type structure ABO_3. (b) Perovskite structure ABO_3 considered as a three-dimensional framework of BO_6 octahedra.

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[1] See, for example, Shirane, Jona, and Pepinsky, Proc. Inst. Radio Engrs. **43**, 1738 (1955).

[2] C. Kittel, Phys. Rev. **82**, 729 (1951).

[3] Shirane, Pepinsky, and Frazer, Acta Cryst. **9**, 131 (1956).

[4] Frazer, Danner, and Pepinsky, Phys. Rev. **100**, 745 (1955).

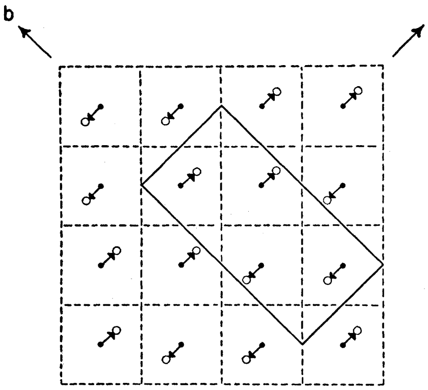

FIG. 2. Antiferroelectric structure of $PbZrO_3$ according to the model of Sawaguchi *et al.*[7]

This paper is concerned with a structural study of the antiferroelectric transition in lead zirconate, $PbZrO_3$.

II. PREVIOUS STUDIES OF LEAD ZIRCONATE, AND SOME DISCREPANCIES

A transition in $PbZrO_3$ occurs at approximately 230°C.[5] From her early x-ray powder diffraction investigation, Megaw[6] proposed tetragonal symmetry at room temperature, with lattice parameters $a_T=4.159$ A and $c_T/a_T=0.988$. Sawaguchi *et al.*[7] pointed out, however, that the powder pattern contains extra lines which can be accounted for by assuming a multiple unit cell of size $4a_T\times 4a_T\times 2c_T$. The true room-temperature symmetry is orthorhombic, with lattice parameters $a=a_T\sqrt{2}$, $b=2a_T\sqrt{2}$, $c=2c_T$.

Single-crystal oscillation photographs were obtained by Sawaguchi *et al.*[7]; and from them these workers concluded that the Pb atoms suffer antiparallel displacements, with respect to their original position in the cubic perovskite lattice, as indicated schematically in Fig. 2. The displacement of the Pb atoms was calculated to be about 0.2 A. The space group was reported to be either $D_{2h}{}^9-Pbam$ or $C_{2v}{}^8-Pba2$, the latter being noncentric. The second choice is in agreement with an extremely small but apparently reproducible piezoelectric effect reported by Roberts[8] from measurements on ceramic disks of $PbZrO_3$.

The hypothesis that all the Pb ions undergo a certain shift along the c axis, in addition to the antiparallel displacement within the ab plane, is apparently in contradiction with the extremely small intensities of the x-ray reflections with odd indices l.[7] Another feature, which strongly indicated the need for a detailed structural study, is the peculiar relation between the orthorhombic a and b axes, $b=2a$, which is the cause for the pseudotetragonality of the crystal. Optical studies by Jona *et al.*,[9] on the other hand, have revealed a large optical—and, indirectly, dielectric—anisotropy within the ab plane, thus confirming the orthorhombic symmetry. Moreover, the characteristic twinning of the crystals clearly establishes the nonpolarity of the ab plane.[9]

A convenient method for growing single crystals of $PbZrO_3$ was found in this laboratory,[9] and a detailed structural analysis of this compound at room temperature appeared both desirable and feasible.

Previous analyses[3,4,10,11] had demonstrated that x-ray techniques alone cannot lead to the structures of these lower-phase pseudoperovskites. This is because the scattering factor of oxygen is generally much smaller than that of the atom A at the origin (e.g., Ba, Pb), so that oxygen contributions to the intensities of the diffracted waves are overwhelmed by the massive contribution of the A atoms. Similar studies were successful only when x-ray information was supplemented by neutron scattering data. In the case of neutron scattering, the structure factor of oxygen is of the same order of magnitude as that of the A atoms.

A single-crystal neutron diffraction study of $PbZrO_3$ was excluded *a priori*, since the size of available untwinned single crystals was much too small for the purpose. It was hoped that a powder neutron diffraction pattern would provide the additional information necessary for a complete solution of the structural problem. This proved to be the case.

III. NEW X-RAY INVESTIGATION

The room-temperature lattice constants of $PbZrO_3$ were first examined via an x-ray powder diffraction photograph of very pure ceramic material, taken with Cu $K\alpha$ radiation. The pseudotetragonal parameters were determined from the high-angle lines derived from the cubic line $N=26$, the tetragonal indexing of which became (105), (501), (134), and (413); the results were $a_T=4.161$ A, $c_T=4.110$ A, and $c_T/a_T=0.988$. These are in good agreement with Megaw's results.[5] The orthorhombic parameters are therefore:

$$a=a_T\sqrt{2}=5.884\text{ A},$$
$$b=2a_T\sqrt{2}=11.768\text{ A},$$
$$c=2c_T=8.220\text{ A}.$$

Single crystals of $PbZrO_3$, grown by the method previously reported,[9] were selected under the polarizing microscope for absence of twins and for regular rectangular shape. Weissenberg patterns were taken with Mo $K\alpha$ radiation filtered by 0.04 mm Zr foil; rotations were about the a, b, and c axes, and about the [210] axis, corresponding to the original cubic [100] direction.

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[5] S. Roberts, J. Am. Ceram. Soc. **32**, 63 (1950).

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

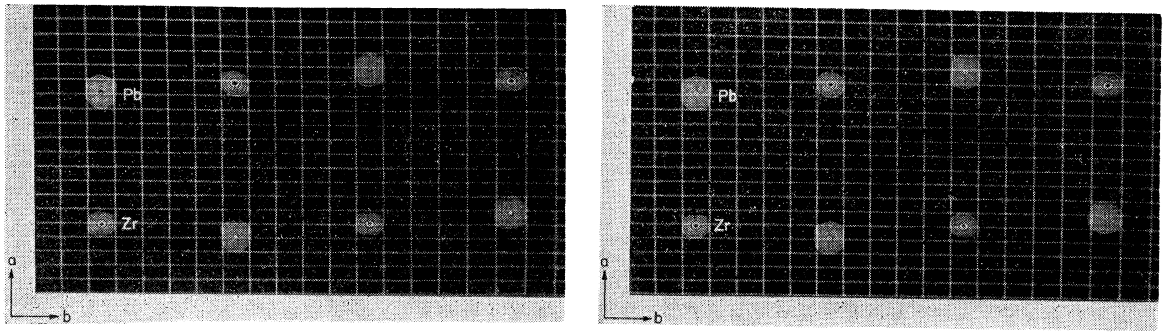
[7] Sawaguchi, Maniwa, and Hoshino, Phys. Rev. **83**, 1078 (1951).

[8] S. Roberts, Phys. Rev. **83**, 1078 (1951).

[9] Jona, Shirane, and Pepinsky, Phys. Rev. **97**, 1584 (1955).

[10] W. Känzig, Helv. Phys. Acta **24**, 175 (1951).

[11] H. T. Evans, Jr., Technical Report No. 58, Laboratory for Insulation Research, Massachusetts Institute of Technology, 1953 (unpublished).



Observed

Calculated

FIG. 3. Observed and calculated electron density projections of $PbZrO_3$ along [001].

Intensities were visually estimated, using the multifilm technique with a calibrated intensity scale. Brass sheet of about 0.02 mm thickness was placed between successive films, to reduce the film-to-film transmission factor. Exposure times varied between eight days and three weeks, depending on the crystal size (see below).

The quantitative analysis was performed only on the projections obtained from reflections of the type $(hk0)$ and $(h,2h,l)$, because it is only in these cases that a reliable absorption correction could be performed without prohibitive efforts. (The linear absorption coefficient for Mo $K\alpha$ radiation is $\mu = 714\ \text{cm}^{-1}$.) Because of their pseudocubic habit, crystals can be found with uniform rectangular cross sections with respect to the [001] and [210] axes, and these cross sections can be determined accurately by microscopic measurements. The crystal used for the $(hk0)$ projection had a cross section of $33\times 41\mu^2$ (length 60μ); that used for the $(h,2h,l)$ projection had a cross section of $36\times 71\mu^2$ (length $100\ \mu$). The absorption corrections were applied according to the graphical method reported by Howell.[12] The values of the absorption factor were computed for 52 points of the reciprocal lattice, and graphs plotted; from these the values for individual reflections could be read by interpolation.

The problem of space group assignment appeared particularly critical. The observed extinction rules satisfy not only the requirements of the space groups *Pbam* and *Pba*2, as proposed by Sawaguchi *et al.*,[7] but also those of the space groups *Pbnm* and the corresponding polar $Pbn2_1$. In fact, the absences attributable to the glide plane perpendicular to the b axis cannot be distinguished in the four cases, in spite of very long exposure times; reflections of the type $(h0l)$ are observed only when both h and l are even. It should be noted, however, that the problem disappears for the projection along the [001] direction (reflections of the type $hk0$). This projection is the same whatever space group is chosen among the four listed above.

Patterson maps were first obtained, on X-RAC, for the projections along [001] and [210]. The former confirmed qualitatively the model given for this structure by Sawaguchi *et al.* A first set of x and y coordinates for Pb and Zr was chosen, leaving the oxygens unshifted, and a structure factor calculation performed. Structure factors F_{hk0} were computed for 302 reflections, up to a value of $\sin\theta/\lambda = 1.26$; the number of the reflections with nonzero observed intensity was 139. For the scattering factors of the atoms involved, the values tabulated in the *Internationale Tabellen* (1944) were used. Dispersion corrections were applied to the scattering factors of Pb and Zr for Mo $K\alpha$ radiation, according to the tables published by Dauben and Templeton.[13]

The x and y coordinates of Pb and Zr were then refined at first by trial and error using the disagreement factor $R = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$ as a criterion, and then by the conventional Fourier method. Figure 3 shows a comparison between observed and calculated electron density projections along [001], involving Pb and Zr atoms only. Finally, a least-squares analysis was carried out, yielding the following values for the coordinates of the heavy atoms, in fractions of the cell edges:

$$x_{\text{Pb}} = 0.706, \quad y_{\text{Pb}} = 0.127;$$
$$x_{\text{Zr}} = 0.243, \quad y_{\text{Zr}} = 0.124.$$

The results appeared largely insensitive to any variation of the oxygen coordinates, so that no attempt was made to find these coordinates from the x-ray data.

The study of the projection along [210] first raised the problem of the space group assignment. Both the Patterson and the Fourier projections seemed to indicate either a relative shift or an anisotropic thermal oscillation of the Pb atoms along the c axis. In the former case, the space group *Pbnm* (or $Pbn2_1$) is favored, and this was in fact assumed in the early stages of the analysis. However, an accurate study of this and other projections revealed that a z shift of Pb is to be excluded, since the observed reflections with odd index l are extremely faint. This leads to the unequivocal conclusion that the Pb atoms perform an anisotropic vibration along the c axis; but it does not yet permit a choice of the space group from among

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[12] R. G. Howell, Acta Cryst. 3, 365 (1950).

[13] C. H. Dauben and D. H. Templeton, Acta Cryst. 8, 841 (1955).

TABLE I. Comparison between observed and calculated intensities of neutron powder diffraction lines.

Line number	*hkl*	Observed intensities, in counts/min		Calculated intensities		
		(a) First run	(b) Second run	Final model	Oxygen unshifted	All atoms unshifted
0*a*	110	203	190	223	70	0
1	120 002	301	293	291	171	150
1*a*	130 112	256	249	256	117	0
2	200 040 122 210	2672	2746	2681	2450	2556
3*a*	132 221 141 023	731	718	588	0	0
3	113 202 042 230 212	2955	3097	3575	4861	4985
4	151 to 241	5811	5640	5531	6712	7048
4*a*	213 to 143	653	[a]	616	112	0
5	311 to 321	544	[a]	452	341	119
5*a*	251 to 134	528	[a]	505	275	0
6	153 to 243	2717	[a]	3010	1504	1716
6*a*	260 to 115	515	[a]	691	178	0
8	262 to 045	4509	[a]	4539	6644	6995
9	180 to 361	1891	[a]	1758	917	83
10	334 to 273	1016	[a]	952	742	1013
11	344 to 433	1736	[a]	1772	3324	4001
12	372 to 007	1885	[a]	1881	3016	3147
$R=(\Sigma\lvert I_{\text{calc}}-I_{\text{obs}}\rvert)/\Sigma I_{\text{obs}}$ for all lines up to angle $2\theta=54°$				0.07	0.44	0.54

[a] Not recorded.

those listed. The Zr atoms, on the other hand, appear undisplaced along the [001] direction. Structure factors $F_{h,2h,l}$ were computed for 92 reflections, up to a value of $\sin\theta/\lambda=1.22$. The number of nonzero observed reflections was 51, but a large number of them appeared to be affected by extinction. The following conclusions could finally be drawn from the x-ray analysis:

(1) As far as Pb and Zr atoms only are concerned, the structure is centrosymmetric, since a satisfactory agreement between observed and calculated structure factors can be attained in either space group *Pbam* and *Pbnm*.

(2) Neither Pb nor Zr appear to be displaced along the [001] direction with respect to their relative positions in the original perovskite lattice. The Pb atoms, however, vibrate anisotropically along [001].

(3) The positions of the oxygen atoms cannot be determined from the x-ray data.

IV. NEUTRON DIFFRACTION STUDY

As already remarked, the small size of available crystals precluded a single-crystal neutron analysis; and the possibility of solution of the structure via a supplementary neutron powder pattern was explored.

Figure 4 shows a comparison of a powder diffraction pattern (a) obtained from a GE XRD-3 with Cu $K\alpha$ radiation, and (b) that obtained with neutrons at the Brookhaven reactor, on the spectrometer of L. Corliss and J. Hastings. For the latter the transmission method was employed, with a neutron wavelength of 1.064 A. The indices in Fig. 4 refer to the N values ($N=h^2+k^2+l^2$) of the original cubic lines of the perovskite lattice.

Qualitative differences between the x-ray and the neutron patterns are visible at first sight. The most striking features are the ratios of the intensities of the lines 2, 3, and 4. Interesting is also the appearance, in the neutron pattern, of a diffraction line on the low-angle side of line 3, and the disappearance of another on the high-angle side of the same line, as compared with the x-ray pattern.

For the quantitative analysis of the neutron pattern, the intensity data were put on an absolute scale by reference to the (111) reflection of a standard Ni powder sample. The values of the scattering lengths used in the calculations were 0.96, 0.62, and 0.58 for Pb, Zr, and O, respectively.[14] The study was done systematically, by keeping in mind also the conditions required by the x-ray results. The most important conditions are summarized in the following:

(a) Reflections of the type $h0l$: when the index h is odd, the corresponding reflection is *not* observed.

(b) Reflections of the type $0kl$: For l odd: when $k=4n$, the corresponding reflection is *not* observed; when $k=4n+2$, the corresponding reflections are rather

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[14] C. G. Shull and E. O. Wollan, Phys. Rev. **81**, 527 (1951).

strong. However, the reflection 021 appears to have practically zero intensity.

(c) The intensities calculated for *all* the reflections which have zero intensity in the observed powder pattern must be either zero or very small.

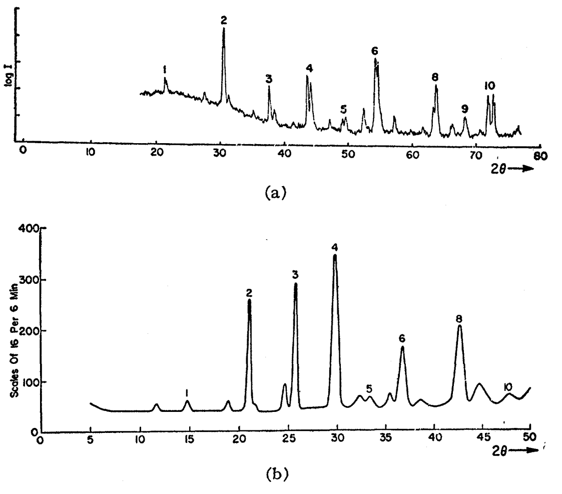
The analysis was accomplished by trial and error. Intensities were computed for 205 reflections. Solutions were sought in each of the possible space groups *Pbam*, *Pba*2, *Pbnm* and *Pbn*2_1. It appeared that all the conditions listed above can be fulfilled only within the space group *Pba*2. As shown in Figs. 5 ff. and as discussed below, the final model involves displacements of the oxygen atoms along the [001] direction. The agreement between observed and calculated intensities (in counts/min) for the powder lines is shown in Table I. A discrepancy factor $R_I=(\Sigma|I_{\text{calc}}-I_{\text{obs}}|)/\Sigma I_{\text{obs}}$ was computed to be 7% for this final model, involving all lines recorded on the neutron pattern up to an angle $2\theta=54°$. For comparison, the intensities were computed also for a structure in which the Pb and Zr atoms alone were shifted according to the results of the x-ray analysis, and the oxygens left undisplaced; the same was accomplished for a fictitious structure in which the displacements δ of all the atoms were set equal to zero. The results of these calculations are shown in the two last columns of Table I. The latter discrepancy factors appeared as 44% and 54%, respectively.

It should be emphasized that the final model satisfies the experimental data not only in the θ regions where diffraction peaks are observed (Table I), but also in those where *no* peaks are recorded.

V. COMBINED NEUTRON AND X-RAY RESULTS

Introduction of the oxygen coordinates obtained from the neutron diffraction analysis into the x-ray data revealed the following:

1. *Reflections of the type hk*0.—The x-ray discrepancy factor R shows practically no change upon introduction of the oxygen coordinates obtained from the neutron study: $R=10.9\%$. A common temperature factor $B=0.53$ A^2 was applied to all atoms in the structure. F_o and F_c synthesis, as well as difference syntheses F_o-F_c, carried out on X-RAC, show that the coordinate parameters are satisfactory, and that in this projection both Pb and Zr have isotropic thermal vibrations. The maps definitely indicate, however, that a larger temperature factor is required for Pb, a smaller one for Zr. Calculations show that upon assuming $B_{\text{Pb}}=0.80$ A^2 and $B_{\text{Zr}}=0.10$ A^2, the discrepancy factor R can be reduced to about 8%. These values of the temperature factors for Pb and Zr are very probably too extreme. No further efforts were made in this direction because it was felt that the accuracy of the observed structure factors was not sufficient for the purpose.



(a)

(b)

FIG. 4. X-ray and neutron powder diffraction patterns of $PbZrO_3$.

2. *Reflections of the type h, 2h, l.*—As stated above, a large number of these reflections appear to be affected by extinction. The electron density maps indicate the existence of an anisotropic vibration of the Pb atoms along the [001] direction. These perhaps account for the fact that the discrepancy factor R for this projection is noticeably higher than in the previous case: $R=18.4\%$. Corrections for extinction and use of an anisotropic thermal factor for Pb could easily reduce the R factor to smaller values. This, however, would not affect the atomic coordinates; and, moreover, the physical significance of the results of these corrections would be highly questionable, in view of the rather limited accuracy of the observed structure factors. The study of thermal vibrations of the atoms in $PbZrO_3$ must await a neutron diffraction analysis of large, untwinned single crystals.

The coordinates of all the atoms for the final model, obtained from the combined x-ray and neutron studies, are given in Table II. In the last column the total shifts of all the atoms are given in angstrom units.

VI. DISCUSSION

Ever since the discovery of the dielectric anomalies in $PbZrO_3$ ceramics[5] suggested the possibility of its

TABLE II. $PbZrO_3$: atomic coordinates.

	Coordinates of the unshifted atoms (in fraction of cell edge)			Final coordinates (in fraction of cell edge)				
Atom	*x*	*y*	*z*	*x*	*y*	*z*	Wyckoff notation	Total shift, in A
Pb′	0.750	0.125	0	0.706	0.127	0	4*c*	0.26
Pb″	0.750	0.125	0.500	0.706	0.127	0.500	4*c*	0.26
Zr′	0.250	0.125	0.250	0.243	0.124	0.250	4*c*	0.04
Zr″	0.250	0.125	0.750	0.243	0.124	0.250	4*c*	0.04
O_1'	0.250	0.125	0	0.270	0.150	0.980	4*c*	0.35
O_1''	0.250	0.125	0.500	0.270	0.100	0.480	4*c*	0.35
O_2'	0	0.250	0.250	0.040	0.270	0.300	4*c*	0.53
O_2''	0	0.250	0.750	0.040	0.270	0.750	4*c*	0.34
O_3'	0	0.500	0.250	0	0.500	0.250	2*b*	0
O_3''	0	0.500	0.750	0	0.500	0.800	2*b*	0.41
O_4'	0	0	0.250	0	0	0.250	2*a*	0
O_4''	0	0	0.750	0	0	0.800	2*a*	0.41

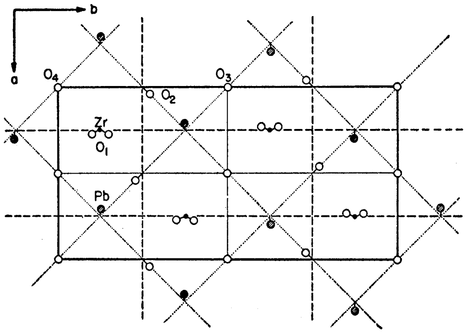


FIG. 5. Schematic projection of the room-temperature structure of $PbZrO_3$ on the (001) plane. The dotted lines represent the projection of the original perovskite unit cells. The heavy solid line shows the orthorhombic unit cell. The dashed lines show the traces of the glide planes.

antiferroelectric character, a number of very intriguing questions were raised, which a structural analysis was expected to answer. It was hoped, for example, that the solution of the structure could shed some light on the reasons for the difference in dielectric behavior of compounds chemically closely related to $PbZrO_3$: for example, ferroelectric $PbTiO_3$. A second—less ambitious but equally intriguing—question is the following: why is the orthorhombic *b* axis, in $PbZrO_3$, exactly equal to 2*a* (i.e., there is no measurable shear distortion of the ideal cubic lattice in the *ab* plane); and yet the typical orthorhombic character is confirmed by a pronounced optical anisotropy of the *ab* plane?[9]

As it turns out, the structural study of $PbZrO_3$ provides a very satisfactory answer to the second question, but cannot of itself give the complete solution of the first. This is because considerations of crystal chemical character (differences in the ionic radii and polarizabilities of Ti and Zr) and internal field considerations play a role of which the structure analysis can unveil the effects but not the causes.

It might be instructive, in this connection, to consider some schematic representations of the structure as depicted in Figs. 5, 6, 7 and 8. Figure 5 represents a schematic projection of the $PbZrO_3$ room-temperature structure on the (001) plane, while the following figures emphasize the distortion of the ZrO_6 octahedra [compare with Fig. 1(b)]. Figure 6 shows a schematic view of only one layer of ZrO_6 octahedra as seen along the [001] direction. Figure 7 represents schematically the ZrO_6 octahedra network as seen along the [100] direction, and Fig. 8 the same as seen along the [010] direction. It appears that the ZrO_6 octahedra distort on zig-zag lines along the original cubic ⟨100⟩ directions, in a way somewhat recalling the pyrochlore-type structure of $Cd_2Nb_2O_7$.[15,16]

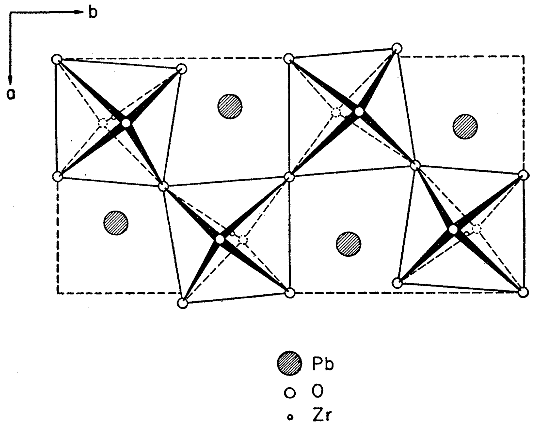


FIG. 6. Schematic view of one layer of ZrO_6 octahedra as seen along [001].

Previous studies of $BaTiO_3$ and $PbTiO_3$ have shown that a lattice expansion takes place in the direction along which the main atomic shifts occur, and a contraction in the direction perpendicular to it. In view of these, the preliminary model of Sawaguchi *et al.*[7] for the structure of $PbZrO_3$ (Fig. 2) could not explain the pseudotetragonality of the lattice ($b=2a$), since an expansion was expected in the direction *a* along which the Pb atoms are displaced (antiparallel to each other). The final model, as illustrated by Fig. 5, provides a satisfactory explanation for the pseudotetragonality, since the oxygens O_1 and O_2 are also found to be displaced in the *b* direction, thus equalizing the parameters along the orthorhombic *a* and *b* axes. This model at the same time explains why a large optical (and consequently dielectric) anisotropy exists within the *ab* plane, which was found to be nonpolar.[9]

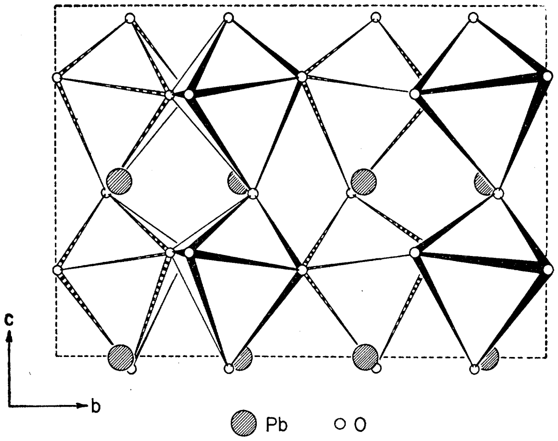


FIG. 7. Schematic view of ZrO_6 octahedra network as seen along [100] direction.

In view of the classification of $PbZrO_3$ as an antiferroelectric material, some features of the crystal structure reported here should be emphasized. It is obvious that $PbZrO_3$ is *not* an antiferroelectric in the sense first introduced, theoretically, by Kittel.[2] Kittel's hypothetical crystal involves two or more sublattices

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[15] A. Byström, Arkiv Kemi, Mineral. Geol. **18A**, No. 21 (1944).

[16] Jona, Shirane, and Pepinsky, Phys. Rev. **98**, 903 (1955).

with equal and opposite polarizations, so that the resulting structure is centrosymmetric; and, among other features, no piezoelectric effect should be detected. As it turns out, $PbZrO_3$ is "antiferroelectric" only in the *ab* plane, since all the atomic shifts within this plane are antiparallel; but it is definitely polar along the *c* direction. The experimental evidence given by Roberts[8] for the existence of a piezoelectric effect in prepolarized ceramic specimens of $PbZrO_3$ agrees with the structural result. Also, the piezoelectric activity is supported by the elastic anomalies of $PbZrO_3$ ceramics at the transition point, as found by Marutake and Ikeda.[17]

It is interesting to note that none of the antiferroelectric crystals whose structures have been studied satisfies Kittel's criterion of centric symmetry. Room-temperature sodium niobate, $NaNbO_3$, belongs to the orthorhombic noncentric space group $P222_1$.[18] Ammonium dihydrogen phosphate, $NH_4H_2PO_4$, assumes symmetry $P2_12_12_1$ in its low-temperature, antiferroelectric phase.[19]

It has been suggested that orthorhombic $PbZrO_3$ could be ferroelectric in the [001] direction, even though accurate tests failed to detect any pyroelectric activity in ceramic samples.[20] Obviously, such a question can be only answered by a detailed study of the dielectric behavior of single crystals, as yet not available in suitable size. But if the crystal were ferroelectric in the *c* direction, the question would immediately arise: why is no sign of ferroelectric activity (i.e., hysteresis loops) ever found in $PbZrO_3$ ceramics, when it is easily detectable in ceramic specimens of (for example) $BaTiO_3$? This is particularly puzzling because we can now compute the maximum contribution to the overall polarization, in the [001] direction of $PbZrO_3$, as given by the ion shifts under the assumption of a purely ionic crystal. This contribution turns out to be of the order of 25 microcoulombs/cm^2, which is of very considerable magnitude. Certainly the assumption of a purely ionic structure is incorrect; but it is known that spontaneous polarizations even 100 times smaller can easily be measured.

We are rather inclined to believe that $PbZrO_3$ is *not* ferroelectric along the [001] direction. This is because the answer to the question, of whether or not the polarity along the *c* axis can be reversed by an applied field, may be anticipated on the basis of the structure. Figures 6, 7, and 8 reveal that the reversal of the *c* axis involves an opposite distortion of the oxygen octahedra and, particularly, *the reversal of the polarizations of the* Pb *sublattices within the (001) plane*. It is conceivable that the amount of energy necessary for such a reversal is very large, and in fact the crystal prefers to assume, under a strong electric field, and very near to the transition temperature, a completely different type of structure (rhombohedral) with ferroelectric properties.[21]

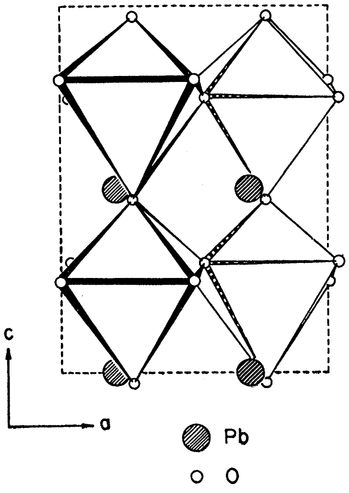

FIG. 8. Schematic view of ZrO_6 octahedra network as seen along [010] direction.

It is interesting, in this respect, to examine the change in bond length brought about by the large shifts of the atoms in $PbZrO_3$. The O—O distances, at room temperature, vary from 2.52 A to 3.28 A, while the sum of the Goldschmidt ionic radii is 2.64 A and the sum of the covalent radii only 1.30 A. Figure 9 shows that the shortest Zr—O distance is that involving the corner of the oxygen octahedron which is on top of the Zr atom. This distance is 1.92 A, which is much shorter than either the sum of the Goldschmidt radii (2.19 A) or the sum of the covalent radii (2.25 A). As for the Pb—O distances, three of them turn out to be very short (two of 2.58 A and one of 2.53 A); the sum of the ionic Goldschmidt radii corrected for 12 coordination is in this case 2.76 A, and that of the covalent radii 2.39 A.

All these short interatomic distances are not new in the literature concerned with the structure of this type of compound. O—O distances as short as 2.49 A (and as long as 3.25 A) were found in the hexagonal modification of $BaTiO_3$ [22]; Pb—O distances as short as 2.53 A

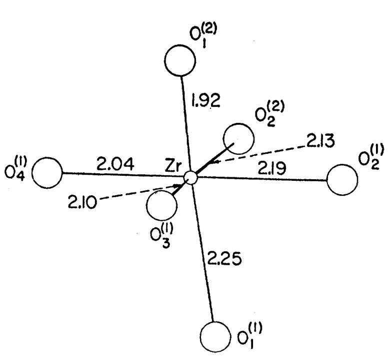

FIG. 9. Environment of Zr in $PbZrO_3$. Interatomic distances are given in A.

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[17] M. Marutake and T. Ikeda, J. Phys. Soc. Japan **10**, 424 (1955).

[18] P. Vousden, Acta Cryst. **4**, 545 (1951).

[19] R. O. Keeling, Jr., and R. Pepinsky, Z. Krist. **106**, 236 (1955).

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

[21] G. Shirane and S. Hoshino, Acta Cryst. **7**, 203 (1954).

[22] R. D. Burbank and H. T. Evans, Jr., Technical Report No. 12, Laboratory for Insulation Research, Massachusetts Institute of Technology, 1948 (unpublished).

were found in the room-temperature structure of $PbTiO_3$.[3] Particularly these short Pb—O bonds, in $PbZrO_3$ as well as in $PbTiO_3$, indicate that the homopolar bond system plays an important role. Megaw[23] predicted that in $PbZrO_3$ the same pyramidal environment of Pb should be achieved which obtains in tetragonal PbO, where the Pb—O bonds form a flat tetragonal pyramid with Pb at the apex. Such a pyramidal environment was, in fact, found in the room-temperature structure of ferroelectric $PbTiO_3$,[3] but does not occur in $PbZrO_3$. In the latter, if we need such a model at all, the shortest Pb—O bonds rather form a flat triangular pyramid with Pb at the apex. The distance between the oxygens at the corner of such a pyramid are 2.89 A, 2.88 A, and 2.75 A. The direction of the normal from the Pb atom to the plane of these three oxygens is approximately that of the [111] direction in the original cubic lattice; this may be related to the fact that a strong electric field induces, in the vicinity of the transition temperature, a ferroelectric phase which was proved to be rhombohedral.[21] It would also be interesting to determine whether such a type of pyramidal environment of the Pb atoms occurs in the as yet unknown structure of the orthorhombic modification of PbO.

Tables of Observed and Calculated Intensities and Structure Factors

Three tables of observed and calculated diffraction data have been prepared[24]: Table III: Observed and Calculated Neutron Powder Diffraction Data for $PbZrO_3$. Table IV: $PbZrO_3$: Comparison Between Observed and Calculated Structure Factors F_{hk0}. Table V: $PbZrO_3$: Comparison Between Observed and Calculated Structure Factors $F_{h,2h,l}$.

VII. ACKNOWLEDGMENTS

The authors are grateful to Dr. L. Corliss and Dr. J. Hastings of the Department of Chemistry, Brookhaven National Laboratory, for obtaining the excellent neutron powder data as illustrated in Fig. 4(b).

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[23] H. D. Megaw, Acta Cryst. 7, 187 (1954).

[24] These tables have been deposited as Document No. 5074 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C., U. S. A. A copy may be secured by citing the document number and by remitting \$3.75 for photoprints or \$2.00 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

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Neutron Diffraction Study of Orthorhombic $BaTiO_3$†

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The atomic positions of ferroelectric $BaTiO_3$ in its orthorhombic phase have been determined by a single-crystal neutron diffraction analysis. Pillar-shaped crystals with their major axes along the cubic [110] direction were maintained as single domains by the application of an electric field. The structure deduced can be viewed as a framework of slightly distorted oxygen octahedra, in which the central Ti ions are displaced towards one of the octahedron edges (polar axis) by 0.13 A. The Ba ions are also shifted in the same direction but by the smaller amount of 0.07 A. A comparison of this structure with that of the tetragonal phase suggests the essential role of Ti in the ferroelectricity of this crystal as treated by Slater.

I. INTRODUCTION

It is well known that $BaTiO_3$ exhibits three ferroelectric phases.[1,2] Possessing a cubic perovskite structure at high temperatures, $BaTiO_3$ transforms to a tetragonal modification at its Curie temperature around 120°C. Upon further cooling, the symmetry changes to orthorhombic at 5°C and to rhombohedral at −80°C. The dielectric anomalies at these transitions, as well as the associated changes in other physical properties, have been well established.

A knowledge of the exact atomic positions in the three phases is of fundamental importance to the understanding of the ferroelectric behavior of $BaTiO_3$. The first steps taken in this direction were the careful x-ray studies of the tetragonal phase carried out by Kaenzig[3] and by Evans.[4] Although the structure of $BaTiO_3$ is very simple, it appeared that reliable information of the atomic positions cannot be given by x-ray analysis. This is a consequence of the small

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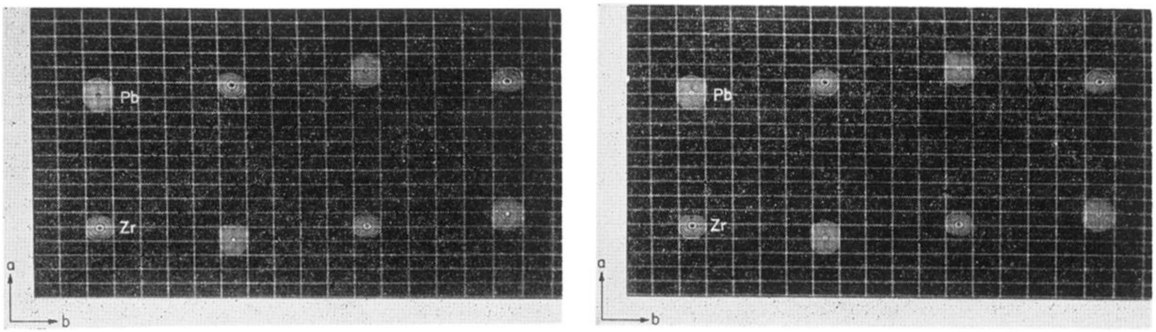
† Development supported by Brookhaven National Laboratory, the U. S. Atomic Energy Commission, the Air Force Office of Scientific Research, and the Signal Corps Engineering Laboratory. X-RAC and S-FAC calculations are supported by the Office of Naval Research.

[1] H. F. Kay and P. Vousden, Phil. Mag. 40, 1019 (1949).

[2] P. W. Forsbergh, Jr., Phys. Rev. 76, 1187 (1949).

[3] W. Kaenzig, Helv. Phys. Acta 24, 175 (1951).

[4] H. T. Evans, Technical Report No. 58, Laboratory for Insulation Research, Massachusetts Institute of Technology, January, 1953 (unpublished).



Observed

Calculated

FIG. 3. Observed and calculated electron density projections of $PbZrO_3$ along [001].