Progress Report

**FERROELECTRIC PROPERTIES OF BISMUTH
FERRATE AND RELATED MATERIALS**

MASTER

Submitted by
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Abstract

Neutron diffraction measurements have been made on pure BiFeO_3 and some solid solutions containing BiFeO_3 . The results for BiFeO_3 above its Neel temperature showed two peaks which could not be indexed on the basis of a simple rhombohedral cell, and which are very unlikely to be caused by impurities. Smaller peaks were found at the same angles in a rhombohedral perovskitic modification in the $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ system, and it seems likely that this material and BiFeO_3 have similar superstructures. It was not possible, however, to determine the atomic coordinates of either material.

The neutron diffraction pattern was best fit with the assumption of a non-centrosymmetric point group. Some purified BiFeO_3 was supplied to Dr. Steward Kurz (Bell Telephone Laboratories), who found that it was capable of frequency doubling in a laser beam. This result proves that BiFeO_3 is definitely non-centrosymmetric.

Neutron diffraction patterns were also obtained for solid solutions in the BiFeO_3 - PbZrO_3 system. It was found that superstructure peaks could be found in the compositional region which appears almost cubic to x-ray diffraction, but which is known to be ferroelectric. Apparently the displacements of oxygen atoms from cubic symmetry are responsible for the ferroelectricity.

Some experiments were conducted using $\text{PbO} \cdot \text{SnO}_2$, in place of PbZrO_3 , as an additive to BiFeO_3 - PbTiO_3 . The effects were similar, but there was more difficulty with impurity phases and incomplete reaction when the tin oxide was used.

A Mossbauer study on $(\text{BiFeO}_3)_{.70} - (\text{PbTiO}_3)_{.30}$ showed a nuclear quadrupole splitting similar to that in BiFeO_3 . Chemical techniques were developed for preparing small quantities of ^{57}Fe enriched solid solutions for further Mossbauer spectroscopy.

Technical Progress

Introduction

The dielectric and magnetic nature of the perovskitic compound, BiFeO_3 , has continued to be an unresolved problem, in spite of considerable efforts, in this country and abroad, to understand the material. Much of the difficulty is caused by impurities formed during the process of making BiFeO_3 . A technique discovered on this project for making relatively pure BiFeO_3 has been published recently¹ and may assist in clarifying some of the effects reported in the literature.

Aside from the impurity problem, two other factors accounting for the difficulty in establishing a definitive category for BiFeO_3 are the high electrical conductivity of the material and the lack of single crystals of suitable size and perfection. The approach on this project to circumvent the conductivity has been to make measurements at the highest frequency where results of interest can be obtained. A forthcoming publication² gives the results obtained, and shows a dielectric anomaly, either ferroelectric or antiferroelectric, at temperatures above 800°C for materials containing 90% BiFeO_3 . This is extremely strong evidence that ferroelectricity or antiferroelectricity is found in BiFeO_3 itself.

Recently, Tomashpol'skii, Venevtsev, and Zhdanov³ have published an analysis of the atomic structure of BiFeO_3 , based on electron diffraction and x-ray diffraction results from a single crystal. The single crystal which was used was 0.8 mm long, and 0.1 to 0.2 mm thick. It was claimed to be single domain. This claim in itself throws considerable doubt on the accuracy of

the results obtained. Based on past experience with similar perovskitic ferroelectrics, single crystals would be expected to be strongly twinned unless electrically treated to remove the twinning. There were some very questionable assumptions made in this article relative to inferring the atomic structure from the x-ray data. In particular, the assumed correction for absorption was highly unrealistic, and really rendered all of the results useless.

The most important progress made on this contract during the past year has been an improved understanding of the possible structures of BiFeO_3 . This has come about through Achenbach's neutron diffraction studies on the material⁴, part of the scheduled effort, and through an unrelated contact. Briefly summarized, Achenbach's work shows that it is almost certain that BiFeO_3 does not have a simple rhombohedral unit cell, but a multiple cell showing superstructure lines (this contradicts the conclusions of Tomashpol'skii et. al.³), in the neutron diffraction pattern. In another development, we furnished some pure BiFeO_3 powder to Dr. S. K. Kurtz at Bell Telephone Laboratories, who determined that it showed optical frequency doubling and, therefore, is non-centrosymmetric. These findings, and other research efforts on this contract, are discussed in greater detail below.

Neutron Diffraction

The material in this section is primarily excerpted from the doctoral dissertation of G. D. Achenbach⁴, with minor reference changes. The section is meant to be indicative of the work done rather than to be complete. Further information can be obtained from the dissertation. An article based on Achenbach's results in neutron diffraction studies of $\text{BiFeO}_3\text{-PbZrO}_3\text{-PbTiO}_3$ is in

preparation. Some of his results are as follows:

"The data taken in the course of this investigation were limited to the three binary systems BiFeO_3 - PbZrO_3 , BiFeO_3 - $\text{PbZr}_{0.5}\text{Ti}_{0.5}\text{O}_3$, and BiFeO_3 - PbTiO_3 and three complementary compositions $\text{Bi}_{2/3}\text{Fe}_{4/9}\text{O}_3$, $\text{PbZr}_{0.9}\text{Ti}_{0.1}\text{O}_3$ and $\text{PbZr}_{0.58}\text{Ti}_{0.42}\text{O}_3$. Much early effort was directed toward the synthesis of single phase polycrystalline BiFeO_3 . The inability to prepare pure BiFeO_3 by direct methods coupled with a desire to refine the BiFeO_3 - PbZrO_3 - PbTiO_3 ternary system led to a thorough structural study of the three binary systems. Compositions vary by 10 mole per cent increments except in special regions where intermediate compositions were of interest."

"Recent high resolution neutron diffraction studies by Plakhtii⁵ of polycrystalline BiFeO_3 at room and high temperatures have proven all previous structural analyses to be incorrect. Diffraction patterns at temperatures between the magnetic ordering temperature and the cubic transition temperature show superlattice peaks not attributable to the simple unit cells proposed. These multiple-cell peaks occur at the angular positions of the magnetic peaks and were not resolved in the initial neutron diffraction studies.

"A nuclear structure which accounts for the superlattice lines visible in neutron diffraction has not been ascertained. However, it must be consistent with data previously reported.

X-ray and electron diffraction data, which reflect only bismuth and iron contributions, show a simple unit cell with the Bi ion at the corner and the Fe ion shifted along the (111) body diagonal. Neutron diffraction data, which reflect oxygen as well as bismuth and iron positions, show superlattice reflections which indicate the true unit cell is a multiple of the simple ABO_3 unit. Compatibility of these data occurs only when the superstructure is associated primarily with oxygen distortion. This type of structure is discussed by Kiselev⁶ and is consistent with the puckered-type oxygen octahedral arrangements known to exist in several perovskitic systems. Recently Kiselev⁷ reported having solved the BiFeO_3 structure using a double cell and finding that the superstructure results from a non-equivalent displacement of the two iron ions. However, no atomic coordinates were given.

"Roginskaya"⁸ proposed that the superlattice lines in the neutron diffraction studies and solid solutions are due to impurities. Single crystal electron and x-ray studies by his group confirm the simple unit cell.

"Plakhtii"⁵ suggested a LaAlO_3 -type doubled cell for BiFeO_3 similar to that found by Buhrer⁹ in the BiFeO_3 - $\text{PbFe}_{0.5}\text{Nb}_{0.5}\text{O}_3$ system.

"Fedulov"^{10,11} reported the first high temperature x-ray and thermal analysis investigations of BiFeO_3 . The "a" parameter increases uniformly whereas "c" remains nearly constant

as the temperature increases to the decomposition point of BiFeO_3 at approximately 800°C . The differential thermal analysis (D. T. A.) curve shows no phase transitions below 850°C . These data show that the Curie temperature of BiFeO_3 does not lie below its decomposition point."

"Neutron diffraction studies by Kiselev^{6,12} and Plakhtii⁵ showed G-type antiferromagnetic ordering of the Fe ions in BiFeO_3 below the 380°C Neel temperature. This magnetic structure is shown in Figure 1 and discussed in detail in the experimental section on BiFeO_3 . Short range magnetic ordering persists to temperatures well above the transition temperature. The intensity of the magnetic peaks follow a Brillouin function with $S = 5/2$; at room temperature, ordering is incomplete and an effective S value of 1.98 was found."

"No attempt was made in this study to determine the nuclear structure of BiFeO_3 from x-ray powder diffraction data alone. Without untwinned single crystals of sufficient size for single crystal x-ray diffraction studies, the exact atomic arrangement cannot be unambiguously ascertained. X-rays are insensitive to the low atomic weight oxygen atoms in the presence of the heavy bismuth and iron atoms. Therefore, atomic structures determined from x-ray data can be considered only as first approximations beyond the assumption of simple cubic positions. The positions of the heavy bismuth and iron atoms determined by x-ray methods should be consistent with the final structure whereas the least squares development of

Figure 1. Temperature difference neutron diffraction pattern and G-type antiferromagnetic structure of BiFeO_3 .

oxygen coordinates is not trustworthy. For this reason, no attempt at final structure solution was made with x-ray powder diffraction data. The published models were simply used as starting points for further refinement by other techniques.

"Neutron powder diffraction studies offer several advantages over x-ray diffraction. The neutron scattering length of heavy atoms such as bismuth or lead is less than twice that of oxygen whereas the same scattering length ratio for x-rays is approximately ten to one. Therefore, while x-ray diffraction intensities are insensitive to oxygen contributions, neutron diffraction patterns reflect the oxygen positions as well as heavier atom positions. Neutron powder diffraction data complement x-ray studies and help alleviate the problem of not having single crystals. The magnetic spin moments of the neutrons will also interact with any magnetic dipoles present in the sample. If the dipoles are randomly oriented as in a paramagnetic state, the magnetic contribution is incoherent, appearing only as an increase in background. If the dipoles are ordered in space, the interaction between the neutron moments and dipoles is regular, thereby creating interference patterns. These magnetic patterns appear superimposed upon the normal nuclear diffraction pattern. For the perovskitic structure, only five possible uniaxially ordered dipole arrangements are possible; one ferromagnetic and four antiferromagnetic. These structures

are analyzed by Wollan and Koehler¹³, who present the general diffraction pattern characteristic of each structure.

"Neutron powder diffraction patterns were made of BiFeO_3 at 77° , 298° , 695° and 880°K . The room temperature (295°K) and high temperature (880°K) patterns are shown in Figure 2. The furnace pattern is subtracted from both patterns to improve clarity and interpretation. The three lower temperature patterns all show an antiferromagnetic structure superimposed upon the nuclear structure. Only the high temperature scan above the magnetic ordering temperature, but well below the decomposition temperature (approximately 1050°K), shows exclusively the nuclear pattern of BiFeO_3 .

"The magnetic pattern is shown by the temperature difference plot in Figure 1. Subtraction of the high temperature pattern from the room temperature pattern cancels all geometric and instrumental effects and reveals only the temperature dependent magnetic structure. The pattern revealed for BiFeO_3 is characteristic of the simple G-type antiferromagnetic structure in which each magnetic Fe ion is surrounded by six antiparallel-aligned Fe ions. The true magnetic cell is double the simple unit cell in all three dimensions. This cell with rhombohedral symmetry is shown in Figure 1. The intensities of the various magnetic peaks indicate the angle between the uniaxial dipole direction and the unique structural (111) direction is 90° . The magnetic dipoles, therefore, lie in the (111) plane but

Figure 2. Room and high temperature neutron powder diffraction patterns of pure BiFeO_3 .

the specific direction in this plane cannot be determined. The anomalous peaks numbered 1, 2, and 3 on the temperature difference pattern result from the shift in nuclear peak position caused by the variation in lattice parameter with temperature.

"The G-type antiferromagnetic structure is best explained by Goodenough's¹⁴ semicovalency model for coupling of magnetic ions through an oxygen anion. The iron (+3) ion, with an outer-electron configuration d^5 , must be assumed to hybridize stable $(d^2 sp^3)$ lattice orbitals. These lattice orbitals are octahedral and can therefore point simultaneously toward all six oxygen near neighbors. The full oxygen anion p orbital which overlaps two iron hybrid orbitals contains two electrons of opposite spin. Since each iron has an oriented net magnetic moment, the electrons do not have an equal probability of being shared by the cations. In accordance with Hund's rule, the anion electron whose spin is parallel to the net cation spin will spend more time on that cation than in the opposite orbital lobe. The anion therefore acts to align in antiparallel fashion the magnetic dipoles of the two cations overlapping a single p orbital. This develops a three dimensional magnetic array of the G-type in which the dipole moment of each iron is surrounded by six antiparallel dipoles.

"The variation in the (111) magnetic peak intensity with temperature is shown in Figure 3. At low temperatures the integrated intensities follow Van Vleck's¹⁵ Brillouin model well. The

Figure 3. Temperature dependence of the magnetic ordering in BiFeO₃.

Brillouin function was evaluated using the experimentally determined 370°C Neel temperature of Latham¹⁶ and the theoretical S value of iron (+3), 5/2. Short range ordering persists with G-type arrangement to nearly 150° above the Neel temperature. Because of its short range nature, the ordering above the Neel temperature is not evident by direct magnetic measurements but can be observed by neutron diffraction.

"The 607°C neutron diffraction pattern of BiFeO₃ (Figure 2) shows peaks at 25 and 42° of 2θ which cannot be generated by a simple ABO₃ unit cell. Comparison of Figures 2 and 4 shows that these peaks cannot be attributed to Bi₂Fe₄O₉ as suggested by Roginskaya⁸. The major peak of Bi₂Fe₄O₉ does occur at approximately 25° of 2θ which could be used as evidence to prove the extra peaks result from impurities present and not superstructure. However, the presence of this peak would require the presence of the other peaks of the sample at their relative intensities. The complete absence of other peaks characteristic of Bi₂Fe₄O₉ confirm x-ray evidence of sample purity and prove BiFeO₃ does possess a superstructure.

"An extensive effort was directed toward the development of an atomic structure for BiFeO₃. A rhombohedral unit cell of twice the volume of the simple ABO₃ cell was found to yield reflections at the positions of the known superlattice peaks. The

Figure 4. Room and high temperature neutron powder diffraction patterns of $\text{Bi}_2\text{Fe}_4\text{O}_9$.

translated cell parameters and ideal atomic positions of this double cell are shown in Table I. This unit cell was used for all subsequent work to find an atomic model consistent with both x-ray and neutron diffraction data.

Table I
The Ideal Double Cell Investigated for BiFeO_3

Parameters: $a = 5.630 \text{ \AA}$, $\alpha = 59^\circ 30'$

Atom	x	y	z
Bi-1	0.250	0.250	0.250
Bi-2	0.750	0.750	0.750
Fe-1	0.000	0.000	0.000
Fe-2	0.500	0.500	0.500
Ox-1	0.250	0.250	0.750
Ox-2	0.250	0.750	0.250
Ox-3	0.750	0.250	0.250
Ox-4	0.750	0.750	0.250
Ox-5	0.750	0.250	0.750
Ox-6	0.250	0.750	0.750

"The summety of space group $R3m$ was initially applied to the unit cell. The atomic shift of the Fe ion reported by Tomashpolskii¹⁷ for a simple cell was used as an initial assumption. The Bi ions were not shifted but allowed to define the position of the cell. Both parallel and anti-parallel shifts of the Fe were used in conjunction with many types of oxygen octahedra distortion. All of these attempts to produce the visible superlattice peaks resulted in the simultaneous generation of a (111) reflection at 13.6° of 2θ . The high temperature neutron diffraction data, as listed in Table II, give no evidence for this peak.

"The cell symmetry was reduced to R3 for subsequent calculations. The mirror in the R3m space group forbids asymmetric shifts of atoms from the (111) plane. This type distortion is necessary to reduce the intensity of a (111) peak. All attempts failed to reduce the (111) reflection intensity to a level which could be considered negligible above background by variation of atomic positions. A structural model generating the correct neutron diffraction pattern could not be found.

Table II

High Temperature Neutron Diffraction Data for BiFeO_3

<u>Two Theta Location</u>	<u>Observed Densities</u>		
	<u>Total Counts</u>	<u>Furnace Counts</u>	<u>Corrected Counts</u>
14.2	2524	2980	0
15.8	16729	0	16729
22.3	36401	0	36401
26.3	10796	0	10796
27.6	13513	1434	12079
28.6	2835	2916	0
30.2	11658	8480	3178
31.8	43155	0	43155
35.6	30456	2730	27726
39.4	37781	0	37781
41.8	2092	0	2092
45.7	24291	0	24291
48.2	24050	0	24050

In a recent publication Tomaspol'skii³ again made the claim that the extra lines in the neutron diffraction pattern of BiFeO_3 are due to an impurity, rather than being superstructure. It is noteworthy that the impurity was no longer

identified, though previously it had been claimed to be $\text{Bi}_2\text{Fe}_4\text{O}_9$. BiFeO_3 is such a difficult material to prepare that a claim of an unknown impurity phase can be made, and it is hard to refute. On the basis of Achenbach's work, however, the impurity phase appears quite improbable.

Further, evidence that the extra lines in the BiFeO_3 neutron diffraction pattern were superstructure and not an impurity phase was found by Achenbach in a neutron diffraction study of the lead zirconate-lead titanate system. In part of this phase diagram, superstructure lines very similar in location to those observed in BiFeO_3 appear in a low-temperature rhombohedral phase. It would be an extraordinary coincidence if these lines were to appear in the rhombohedral lead zirconate-lead titanate as superstructure and in rhombohedral BiFeO_3 as an impurity.

Lead Zirconate-Lead Titanate (Neutron Diffraction)

Achenbach's neutron diffraction work on lead zirconate-lead titanate is as follows:

"The preliminary phase diagram for the BiFeO_3 - PbZrO_3 - PbTiO_3 ternary system prepared by Clarida¹⁸ shows the rhombohedral phase region extending from pure BiFeO_3 between the tetragonal and orthorhombic regions completely to the PbZrO_3 - PbTiO_3 binary system. These data indicate the rhombohedral structures of the PbZrO_3 - PbTiO_3 system to be isostructural to BiFeO_3 . Cook¹⁹ reported the rhombohedral region of the PbZrO_3 - PbTiO_3 system actually includes two rhombohedral structures, the difference in which can only be detected by electrical measurement.

The structural investigation of the $\text{PbZr}_{0.5}\text{Ti}_{0.5}\text{O}_3$ - BiFeO_3 system yielded data showing a rhombohedral structure of low distortion occurring in the central area of the ternary diagram. These data place the existence of a continuous rhombohedral region in doubt.

"Cook provided a series of powdered samples from the PbZrO_3 - PbTiO_3 system for our further investigation. The samples contained a binder which was removed by a 24 hour anneal at 700°C . Two samples, $\text{PbZr}_{0.9}\text{Ti}_{0.1}\text{O}_3$ and $\text{PbZr}_{0.58}\text{Ti}_{0.42}\text{O}_3$ were selected for study. The $\text{PbZr}_{0.58}\text{Ti}_{0.42}\text{O}_3$ composition is centered in the varrow arm of the 'high temperature' rhombohedral phase at room temperature (see Figure 5). Cook²⁰ suggested study of the $\text{PbZr}_{0.9}\text{Ti}_{0.1}\text{O}_3$ composition because his work showed this sample to be more characteristic of the 'low temperature' rhombohedral phase than a more centered composition.

"X-ray powder diffraction patterns were prepared on the two samples to confirm structural parameters. Both patterns were indexed on a simple rhombohedral unit cell with the following parameters:

$$a = 4.130 \text{ \AA} \quad \alpha = 89^\circ 44'$$

$$a = 4.070 \text{ \AA} \quad \alpha = 89^\circ 39'$$

Only one small peak with $3.23 \text{ \AA}$ d-spacing in the pattern of $\text{PbZr}_{0.9}\text{Ti}_{0.1}\text{O}_3$ gives indication of a difference in atomic structure. This

Figure 5. Phase diagram of the PbZrO_3 - PbTiO_3 system by Cook (1966a).

peak occurs at the exact location of the major peak of a TiO_2 phase and very near the position of several other titanium and lead compounds which could form in the preparation of $\text{PbZr}_{0.9}\text{Ti}_{0.1}\text{O}_3$. Therefore, this single peak cannot be used as conclusive evidence of superstructure or two different rhombohedral structures.

"Room temperature neutron diffraction patterns were prepared on the $\text{PbZr}_{0.9}\text{Ti}_{0.1}\text{O}_3$ and $\text{PbZr}_{0.58}\text{Ti}_{0.42}\text{O}_3$ samples to complement the x-ray studies. Sketches of the two patterns appear in Figures 6 and 7. The patterns are similar except for intensity variations and the presence of the two small peaks at 25.3° and 40.3° of 2θ in the $\text{PbZr}_{0.9}\text{Ti}_{0.1}\text{O}_3$ pattern. Intensity data taken on the nickel standard allow the intensity calculations to be placed on an absolute basis. No absorption data were taken; therefore, the absorption corrections were calculated by averaging the linear absorption corrections of the constituent elements in proportion to mass fraction as discussed by Bacon²¹. This technique may reduce absolute accuracy but keeps structural calculations for the two compositions on a correct relative basis.

"No attempt was made at complete solution of the atomic structure. Structural calculations were made only to corroborate or negate the work of Cook suggesting the two rhombohedral regions in the PbZrO_3 - PbTiO_3 phase diagram. The structural calculations were based on the R3m space group which is consistent

Figure 6. Sketch of room temperature neutron powder diffraction pattern of $\text{PbZr}_{0.9}\text{Ti}_{0.1}\text{O}_3$.

Figure 7. Sketch of room temperature neutron powder diffraction pattern of $\text{PbZr}_{0.58}\text{Ti}_{0.42}\text{O}_3$.

with x-ray and electrical data. Cell parameters determined by x-ray analysis were used in the calculations. A temperature factor of 1.0 was used for all atoms. The structural parameters and atomic coordinates for both assumed structures are given in Table III. The lead atom is shifted slightly along the (111) direction as suggested by Cook.

Table III

Assumed Atomic Structures for

$\text{PbZr}_{0.9}\text{Ti}_{0.1}\text{O}_3$				$\text{PbZr}_{0.58}\text{Ti}_{0.42}\text{O}_3$			
$a = 4.130 \text{ \AA} \quad \alpha = 89^\circ 44'$				$a = 4.070 \text{ \AA} \quad \alpha = 89^\circ 39'$			
<u>x</u>	<u>y</u>	<u>z</u>	<u>ATOM</u>	<u>x</u>	<u>y</u>	<u>z</u>	
0.030	0.030	0.030	Pb	0.030	0.030	0.030	
0.500	0.500	0.500	B	0.500	0.500	0.500	
0.500	0.500	0.000	O ₁	0.500	0.500	0.000	
0.500	0.000	0.500	O ₂	0.500	0.000	0.500	
0.000	0.500	0.500	O ₃	0.000	0.500	0.500	

"The experimental and calculated intensities for all peaks of $\text{PbZr}_{0.9}\text{Ti}_{0.1}\text{O}_3$ and $\text{PbZr}_{0.58}\text{Ti}_{0.42}\text{O}_3$ are compared in Table IV. Because all calculated intensities are lower than the respective experimental values, the absorption corrections calculated are probably too large. The relative differences between calculated and experimental intensities indicate the atoms, particularly the oxygen, are shifted significantly from the ideal positions assumed.

Table IV

Neutron Diffraction Intensities for

$\text{PbZr}_{0.9}\text{Ti}_{0.1}\text{O}_3$			$\text{PbZr}_{0.58}\text{Ti}_{0.42}\text{O}_3$		
Angle 2θ (deg)	Intensities		Intensities		Angle 2θ (deg)
	Expt.	Calc.	Expt.	Calc.	
15.20	4345	798	852	3612	15.40
21.55	18572	11159	6081	11489	21.85
25.30	2013				
26.50	31843	27641	41293	56002	26.90
30.70	43405	33130	31348	46412	31.10
34.30	9422	2099	1895	9117	34.80
37.80	19598	6936	6088	14137	38.30
40.30	717				
43.90	33508	29770	28059	34544	44.60
46.50	10820	2268	1986	7060	47.30
49.40	5743	3892	2577	4245	50.10
52.00	10291	18070	26952	25575	52.90
54.50	10645	11944	11216	12753	55.30
56.70	6471	1624	1402	5835	57.50

"The simple cell structure generates all diffraction peaks except the two minor peaks in the $\text{PbZr}_{0.9}\text{Ti}_{0.1}\text{O}_3$ pattern. Neither of these peaks corresponds to the extra small peak in the x-ray pattern of the sample and therefore must result from atomic superstructure. The increased proportion of the negative titanium scattering length in the average scattering length used for the B-site atom alters calculated intensities markedly. The change in calculated intensity varies directly as the change in experimentally determined intensity for seven of the twelve peaks. For the other five peaks the variation

in calculated intensities is opposite that found experimentally. The variation in nuclear scattering length of B-site atom could possibly cause the two superlattice peaks to disappear without a structural change, but this must be considered improbable in light of the other intensity variations in the same samples.

"A conservative evaluation of the x-ray and neutron powder diffraction data from the two samples indicates $\text{PbZr}_{0.9}\text{Ti}_{0.1}\text{O}_3$ definitely possesses a multiple-cell structure whereas $\text{PbZr}_{0.58}\text{Ti}_{0.42}\text{O}_3$ probably has a distorted simple unit cell. This is consistent with Cook's interpretation of his electrical data. This work does not confirm the location of his proposed boundary between the two rhombohedral regions because it only indicates the phase transition at room temperature lies somewhere between the two compositions studied. Thermodynamic considerations favor higher crystal symmetry at higher temperature. The proposed multiple-single cell relationship is thereby thermodynamically compatible with Cook's phase diagram.

"The neutron diffraction data on these two zirconate-titanate compounds provide no conclusive evidence regarding the continuity of the rhombohedral phase region across the ternary system. The high temperature rhombohedral phase of the PbZrO_3 - PbTiO_3 does not possess superstructure isomorphous to BiFeO_3 . The low temperature rhombohedral region does possess a multiple-cell structure

with its superlattice peaks occurring at the same angular positions as those of BiFeO_3 . Determination of the degree of similarity between the BiFeO_3 rhombohedral phase and the low temperature $\text{Pb}(\text{ZrTi})\text{O}_3$ rhombohedral phase awaits solution of either of the structures. With the structure of BiFeO_3 solved, for example, the proper exchange of scattering lengths in the intensity calculation is all that would be required to generate the intensities for an isostructural $\text{PbZr}_{0.9}\text{Ti}_{0.1}\text{O}_3$. If only minor atomic shifts were needed to develop the proper neutron diffraction pattern for $\text{PbZr}_{0.9}\text{Ti}_{0.1}\text{O}_3$ the two structures would belong to the same phase region with only a diminution in distortion evident in the central region of the ternary diagram. With present data, the continuity of the two rhombohedral regions is uncertain, but must be considered improbable."

Achenbach has thus pointed out that a solution to the atomic structure of BiFeO_3 (fitting the neutron diffraction data), could be found if the structure were known for the low-temperature rhombohedral lead zirconate-lead titanate. The latter is a feasible research problem, because small (~ 1 mm.) single crystals of the material are available, although these tend to display ferroelectric twinning.

Frequency Doubling - BiFeO_3

In 1961 Franken discovered that, owing to the intense electric field at optical frequencies generated in a laser beam, it was possible to achieve

frequency conversion of optical radiation in quartz. The second harmonic frequency, 2ω , of incoming light at frequency ω , is found when an electronic polarization, $P_i^{2\omega}$, is generated by electric fields E_j^ω and E_k^ω , according to

$$P_i^{2\omega} = d_{ijk} E_j^\omega E_k^\omega$$

where $P_i^{2\omega}$ = electronic polarization, component i , frequency 2ω .

E_j^ω = electric field, component j , frequency ω .

E_k^ω = electric field, component k , frequency ω .

Repeated indices, i, j, k , are summed according to the Einstein summation convention.

The tensor d_{ijk} is zero for centrosymmetric materials.

A technique for measuring the second harmonic generation from powders of crystalline material (most of the work in this field is done with single crystals) was developed by Dr. S. K. Kurtz, at Bell Telephone Laboratories. We supplied him with a sample of our single-phase BiFeO_3 . He found that it showed appreciable second harmonic generation, and therefore, BiFeO_3 must be non-centrosymmetric.

While the above finding limits the space groups to which BiFeO_3 may belong (to $R3$, $R3m$, and $R32$), it does not clarify the question of whether BiFeO_3 is ferroelectric or antiferroelectric. Only the groups $R3$ and $R3m$ permit ferroelectricity, but antiferroelectricity, as it has been customarily defined, may exist in any of the groups above.

BiFeO₃ - PbZrO₃ (Neutron Diffraction)

Achenbach⁴ made an extensive study of the neutron diffraction patterns of solid solutions in the BiFeO₃ - PbZrO₃ system. The data taken and their interpretation are too lengthy to report here, but an article based on this study is in preparation. The study confirms the existence of distortion in the oxygen octohedron in perovskitic solid solutions where the heavy metal atoms are essentially in the cubic, non-distorted position. This result had not been previously observed.

Several of Achenbach's neutron diffraction patterns for this solid solution series are given in Figures 8, 9, and 10. It is interesting to compare these with the pattern for a simple-cell perovskite (Figure 7) and with pure PbZrO₃²². It is seen that there is a gradual transition between the two in the series, but none of the solid solutions is completely free of superstructure.

Figure 8. Sketch of the room temperature neutron powder diffraction pattern of $90 \text{ PbZrO}_3 - 10 \text{ BiFeO}_3$.

Figure 9. Sketch of the room temperature neutron powder diffraction pattern of 80 PbZrO₃-20 BiFeO₃.

Figure 10. Sketch of the room temperature neutron powder diffraction pattern of 60 PbZrO₃-40 BiFeO₃.

Solid Solutions Containing Tin Oxide

A considerable amount of preparation effort during the past year was devoted to solid solutions of BiFeO_3 with PbTiO_3 and $\text{PbO} \cdot \text{SnO}_2$. The latter is a compound which does not form under the usual reaction conditions, but which is often referred to as " PbSnO_3 " in solid solutions. It has been extensively used in enlarging the stability range of the anti-ferroelectric phase in perovskites.

The general preparation conditions used in making and analyzing these solid solutions are the same as those used previously in other perovskitic systems. The reaction temperature and time, and the results are given in Table V below. Table VI gives the lattice parameters of some of the solid solutions which could be analyzed.

Examination of Table I reveals that the addition of tin oxide to the pseudo-binary system BiFeO_3 - PbTiO_3 close to the region of maximum distortion (high c/a ratio), the tetragonal 60-40 composition, diminishes the extent of distortion quite markedly. The c/a ratio is reduced from 1.17 for 60 BiFeO_3 - 40 PbTiO_3 to 1.10 for 10% PbSnO_3 - 90% (60 BiFeO_3 - 40 PbTiO_3). For the 20% PbSnO_3 - 80% (60 BiFeO_3 - 40 PbTiO_3) the x-ray pattern is essentially cubic (probably rhombohedral and evidently not single phase).

This behavior corresponds closely to that of the pseudo-ternary PbZrO_3 - BiFeO_3 - PbTiO_3 system. Here again the addition of ZrO_2 leads to a marked reduction in the distortion of the pseudo-binary 60 BiFeO_3 -

Table V

Preparation of BiFeO_3 - PbTiO_3 Perovskite Structures Containing Sn

Sample Number	Composition of Sample	Reaction Conditions		Comments
		Temp. ($^{\circ}\text{C}$)	Time (Hrs.)	
42A	.10 PbSnO_3 -.90 (.60 BiFeO_3 -.40 PbTiO_3)	950	1	Very impure
B	"	1000	1	Nearly single phase
Ca	"	1000	1	--
C	"	1050	1	Nearly single phase
D	"	1050	1	Multiphase
Ea	"	1000	1	--
*E	"	1100	1	Single phase
F	"	1050	3.2	Multiphase
Ga	"	1050	3.2	--
G	"	1050	3.2	Multiphase
43A	.20 PbSnO_3 -.80 (.60 BiFeO_3 -.40 PbTiO_3)	950	1	Very impure
B	"	1050	1.2	Impure
Ca	"	1050	1.2	--
C	"	1100	1	Fused-impure
*D	"	1050	3	Best of A-E, but 10% impurity
Ea	"	1050	3	--
E	"	1050	3	Impure

Table V Cont'd.

Preparation of BiFeO_3 - PbTiO_3 Perovskite Structures Containing Sn

Sample Number	Composition of Sample	Reaction Conditions		Comments
		Temp. ($^{\circ}\text{C}$)	Time (Hrs.)	
44A	.10 PbSnO_3 -.90 (.70 BiFeO_3 -.30 PbTiO_3)	1000	1	Very impure
Ba	"	1000	1	--
B	"	1050	1	Impure
45A	.20 PbSnO_3 -.80 (.70 BiFeO_3 -.30 PbTiO_3)	1000	1	Very impure
Ba	"	1000	1	--
B	"	1050	1	25% impurity, less than A or C
C	"	1050	1	Impure
47A	.10 PbSnO_3 -.90 BiFeO_3	1000	1	Fused
B	"	800	1	Impure-Better than C
Ca	"	800	1	--
C	"	900	1.5	Impure
72A	.10 PbSnO_3 -.90 (.50 BiFeO_3 -.50 PbTiO_3)	975	2	Very impure
B	"	975	2	Slightly impure
Ca	"	975	2	--
C	"	1075	2	Slightly impure
*D	"	1025	2	Nearly single phase

Table V Cont'd.

Preparation of BiFeO_3 - PbTiO_3 Perovskite Structures Containing Sn

Sample Number	Composition of Sample	Reaction Conditions		Comments
		Temp. ($^{\circ}\text{C}$)	Time (Hrs.)	
74A	.10 PbSnO_3 -.90 (.50 BiFeO_3 -.50 PbTiO_3)	975	2	Much more impure than 72B
76A	.10 PbSnO_3 -.90 BiFeO_3	800	2	Impure
Ba	"	800	2	--
B	"	900	2	20% impurity, Best of A-C
C	"	900	2	Impure
77A	.10 PbSnO_3 -.90 (.10 BiFeO_3 -.90 PbTiO_3)	1000	1.5	Impure
B	"	1100	2	Multiphase
Cb	"	800	1	--
*C	"	960	1	Slightly impure
79A	$\text{BiFe}_{0.96}\text{Sn}_{0.03}\text{O}_3$	800	2	Slightly impure
*79A-L	Sample 79A after 4 HNO_3 Leachings	-	-	Bi_2O_3 disappeared, but unidentified impurity at 3.06, 2.65, +2.23 Å increased.

*Sample used for determination of structural parameters.

Table VI

Structural Parameters of BiFeO_3 - PbTiO_3 System With + Without Sn

Sample Composition	Tetragonal			Rhombohedral		Pseudocubic
	<u>c</u>	<u>a</u>	<u>c/a</u>	<u>a</u>	<u>α</u>	<u>a</u>
BiFeO_3				3.958	$89^\circ 30'$	
$\text{BiFe}_{0.96}\text{Sn}_{0.03}\text{O}_3$				3.946	$89^\circ 26'$	
.60 BiFeO_3 -.40 PbTiO_3	4.460	3.818	1.168			
.10 PbSnO_3 -.90 (.60 BiFeO_3 -.40 PbTiO_3)	4.290	3.868	1.109			
.20 PbSnO_3 -.80 (.60 BiFeO_3 -.40 PbTiO_3)						3.978
.50 BiFeO_3 -.50 PbTiO_3	4.388	3.844	1.142			
.10 PbSnO_3 -.90 (.50 BiFeO_3 -.50 PbTiO_3)	4.256	3.879	1.097			
.10 BiFeO_3 -.90 PbTiO_3	3.912	4.182	1.069			
.10 PbSnO_3 -.90 (.10 BiFeO_3 -.90 PbTiO_3)	3.985	3.899	1.022			

40 PbTiO_3 system. As more PbZrO_3 was added, the x-ray patterns became almost cubic and multiphase. The x-ray diffraction patterns for the solid solutions containing zirconium were, however, much sharper than for those containing tin, and the peaks were better resolved. Thus, the overall effect of Sn on crystallographic parameters is similar to that of Zr, but it appears to be considerably easier to prepare solid solutions containing Zr.

It does not appear useful to continue the study of Sn additions to compositions consisting primarily of $\text{BiFeO}_3 - \text{PbTiO}_3$. Considering the similarity in behavior of Sn and Zr, some exploratory work in a system consisting primarily of PbZrO_3 , with additions of BiFeO_3 and " PbSnO_3 ", appears justified.

Dielectric Results

The main effort in the dielectric work, which was conducted by R. T. Smith²³, was summarized in the previous progress report. Smith's doctoral dissertation was subsequently accepted, and an article based on his results is scheduled to appear in the Journal of Applied Physics².

One of the most significant pieces of information obtained by Smith was the existence of dielectric anomalies at about 800°C for solid solutions containing 90 mol % BiFeO₃. With respect to the data on one of these solid solutions, it was puzzling that the measured dissipation factor of the dielectric stayed relatively constant over the temperature range where the real part of the dielectric permittivity was increasing by a factor of about three. It was decided to repeat this measurement using the same sample, though in the new measurement the sample would have been aged about a half year since manufacture and shaping. The results are given in Figure 11. It is seen that in the aged sample, the anticipated drop in dissipation factor does occur. Also the dielectric permittivity is not as high as in the virgin sample, but the dielectric anomaly is still very noticeable.

Mössbauer Effect Research

The program of Mössbauer effect research which had been planned for the current contract period was greatly curtailed because of the illness of the student who was primarily responsible for the measurements. Another student has been assigned to this work, and it is expected to be

more fruitful in the near future. There was also a certain amount of chemical technique which it was necessary to develop in order to prepare the Mössbauer samples. These are enriched with ^{57}Fe , and since this material costs over \$3.00 per milligram, microchemical techniques are definitely necessary in preparing samples. This development work has been done.

A preliminary velocity spectrum was run on one of the solid solutions of interest. Since this measurement is indicative of future efforts, the report, by James P. Canner, is given here:

A velocity spectrum was run on $(\text{BiFeO}_3)_{.70} - (\text{PbTiO}_3)_{.30}$ using a ^{57}Co source diffused in a copper foil. The velocity calibration was made by using the two inner peaks of a natural iron absorber spectrum. The sample was 94 mg. of unenriched 70% BiFeO_3 - 30% PbTiO_3 , which was mixed and pressed into 0.5 gms of bakelite to form a disc 1 inch in diameter and about 0.5 mm thick.

The resulting pattern gave a split central peak indicating no magnetic interaction. (This agrees with Latham's earlier results¹⁶ that the magnetic transition in this material is below room temperature and also very diffuse). The peaks occur at + 0.33 mm/sec and - 0.13 mm/sec. The total splitting can be identified with nuclear quadrupole splitting, giving a value of .46 mm/sec, equivalent to $5.3 \text{ MHz} = e^2 Qq/h$, where

Q = quadrupole moment
 q = electric field gradient

h = Planck's constant

e = electronic charge

From this, the field gradient can be calculated to be 1.21×10^{17} volts/cm² at the nucleus. An anti-shielding factor has been calculated for ⁵⁷Fe, showing that the field gradient at the nuclear site is 10.1 times greater than the average field gradient over the atom. This gives a field gradient at the atom of 1.2×10^{16} volt/cm². A calculated value of the electric field gradient at the atom site for BiFeO₃ was given by Tomashpol'skii and Venevtsev²⁴ as $2-6 \times 10^{16}$ volt/cm, depending on the variation in ionic charges and polarizabilities which one might expect for BiFeO₃. The observed value of the electric field gradient for pure BiFeO₃ was given as 1.4×10^{17} volt/cm at nucleon site. The field gradient is thus somewhat larger for BiFeO₃ than for the solid solution.

The isomer shift or chemical shift is the shift of the center of the Mössbauer pattern from some reference point. Usually #310 stainless steel is chosen as a reference, although, numerous other materials have been cited. Our data indicated an isomer shift of +.10 mm/sec from zero velocity. The natural iron reference-calibration pattern has an isomer shift of -.21 mm/sec from zero. Walker, Wertheim, and Jaccarino²⁵ give an isomer shift of +.15 mm/sec $\pm$.05 for natural iron referenced to #310 stainless steel, so the total shift for the solid solution would be 0.46 mm/sec. (Other references quote values of isomer shift for natural iron of .10 to .12 mm/sec.)

Walker²⁵ also presents a graph from which the isomer shift can be related to the bonding state of the ^{57}Fe atom. Using the above values and assuming the iron to be Fe^{3+} , we get a value for the fraction of 4s electrons of 1.7 to 2.3%.

Pure BiFeO_3 and BaTiO_3 appear to have values of 1.6% and 1.2% respectively, due to isomer shifts of .47 mm/sec and .50 mm/sec. The amount of covalency in the solid solution is seen to be slightly more than that of BiFeO_3 , and significantly more than BaTiO_3 .

Single Crystals

A valid analysis of the atomic coordinates of BiFeO_3 will require, at the very minimum, untwinned single-domain crystals of about 100 micron dimension for x-ray diffraction in addition to the neutron powder diffraction data. It is possible to grow small single crystals of BiFeO_3 , though the amount of twinning in the crystals reported in the literature is uncertain. The growth process is difficult because of the tendency to form $\text{Bi}_2\text{O}_3 \cdot 2\text{Fe}_2\text{O}_3$.

For single crystal neutron diffraction and for ferroelectric studies, larger crystals are needed, with dimensions of the order of millimeters. If the crystal can have its domain twinning removed by electrical means, the growth of multi-domain crystals would not be a serious handicap.

One of the graduate students now working on this project is Christian Michel, who received his Docteur de Troisieme Cycle degree at the University of Grenoble, France. He brought with him some crystals grown by M. Buisson in an attempt to make BiFeO_3 . These crystals were mainly

$\text{Bi}_2\text{O}_3 \cdot 2\text{Fe}_2\text{O}_3$, but there are some changes possible in the growth parameters which should tend to favor the formation of BiFeO_3 . It is expected that co-operation on the growth of these crystals will be continued. M. Buisson has the equipment and general knowledge of growth techniques and will probably do the actual crystal growing, while the group here will do the diffraction and electrical studies.

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Publications

Journal Publications

1. "Dielectric Properties of Solid Solutions of BiFeO_3 with $\text{Pb}(\text{Ti}, \text{Zr})\text{O}_3$ at High Temperature and High Frequency", Robert T. Smith, Gary D. Achenbach, Robert Gerson and W. J. James: Accepted by the Journal of Applied Physics for publication early in 1968.

2. "A Technique for the Preparation of Single Phase, Polycrystalline BiFeO_3 ", G. D. Achenbach, W. J. James, and Robert Gerson, J. Amer. Ceram. Soc. 50, 437 (1967). Preparation of this article was mentioned in last year's progress report, but it had not been accepted.

Doctoral Dissertations

The doctoral dissertations of Gary D. Achenbach, James I. Latham, and Robert T. Smith were accepted by the University of Missouri at Rolla for the June 1967 commencement. The preparation of these dissertations was reported in a previous progress report.

Talks

"Superstructure in the Lead Zirconate - Lead Titanate Solid Solution System", Robert Gerson, W. J. James and Gary D. Achenbach, to be presented at the March 1968 meeting of the American Physical Society (Berkeley, California).

Presented at the March 1967 meeting of the American Physical Society (Chicago, Illinois):

1. "Ferroelectric Properties in Solid Solutions of BiFeO_3 with PbTiO_3 , PbZrO_3 , and $\text{PbTi}_{0.5}\text{Zr}_{0.5}\text{O}_3$ ", Robert T. Smith, Robert Gerson and W. J. James.

2. "Magnetic Properties in Perovskitic Solid Solutions Containing BiFeO_3 ",

James I. Latham, Robert Gerson, and W. J. James.