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Final Report

Ferroelectric Properties of Bismuth Ferrate
and Related Materials

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ABSTRACT*

The main results of the investigations on this contract have been as follows:

- 1) Techniques were developed for the preparation of the perovskite-type compound BiFeO_3 , both as a powder and in small (1 mm) single crystals. The structure of BiFeO_3 was then determined. It is ferroelectric and the space group to which it belongs, $R3c$, permits weak ferromagnetism, opening the possibility for the use of the interaction of electric and magnetic ordering in the material.
- 2) The structure of the low temperature phase of rhombohedral lead titanate zirconate has been found to be similar to that of BiFeO_3 . Both structures involve a rotation of oxygen octahedra about a $\langle 111 \rangle$ axis. This effect is also found in other compounds. It is very strongly developed in LiNbO_3 , and less so in LaAlO_3 and SrTiO_3 .
- 3) Ferroelectric properties were investigated in the system $\text{BiFeO}_3 - \text{PbZrO}_3$. While high Curie points were found in this system, other properties of the materials make their application as piezoelectrics unlikely.
- 4) Mössbauer studies were made on the system $\text{BiFeO}_3 - \text{PbTiO}_3 - \text{PbZrO}_3$. The internal magnetic fields of some of the antiferromagnetic compositions were determined, and a comparison was made of Mössbauer anomalies at ferroelectric and antiferroelectric transitions. This type of investigation also yielded basic information on solid solutions of mixed ferroelectrics.

*Note: The most significant results of the studies completed under this contract have been published. Copies of all of the publications are included as appendices to this summary report. The report has the purpose of correlating the publications and relating their contents to the main investigation.

Summary Report

This project has had as its objective the study of the perovskite BiFeO_3 and some of its solid solutions. When the contract was initiated, the classification and structure of the material were the source of considerable controversy, which continued until recently^{1,2}. Investigators on this contract have now succeeded in classifying BiFeO_3 and in explaining its behavior in terms of a wider group of distorted perovskites³. To do this it was necessary to determine the atomic structure of BiFeO_3 , which was accomplished by using a combination of neutron diffraction of the powder and X-ray diffraction of the single crystal.

At the beginning of the work, there were available neither single crystals nor powders of adequate purity. This meant that, although BiFeO_3 could be classified as a rhombohedral perovskite, and had been shown to be antiferromagnetic⁴, there remained important aspects of its behavior which were not known. For example, it was not known whether the material was ferroelectric, antiferroelectric, or neither, nor whether it exhibited weak ferromagnetism in addition to being antiferromagnetic. The answers to these questions are the determining factors in the possible future utilization of BiFeO_3 in devices. They also lead to an improved understanding of a wide category of materials of present device importance, including LiNbO_3 and the rhombohedral modification of lead titanate zirconate, and therefore much effort has been expended in exploring these questions. It was found that BiFeO_3 is ferroelectric, although with a high electric coercive field^{3,5}, and that its space group, unequivocally determined

as R3c, permits weak ferromagnetism. Weak ferromagnetism has not, however, been observed in powders in pure BiFeO_3 .

The determination of the atomic structure of BiFeO_3 by neutron diffraction was hindered by the relatively large impurity peaks in the diffraction pattern due to $\text{Bi}_2\text{Fe}_4\text{O}_9$, a compound normally formed with BiFeO_3 when the latter is made by the reaction of bismuth and ferric oxides. A process was developed in which the formation of $\text{Bi}_2\text{Fe}_4\text{O}_9$ was avoided through the use of a large excess of Bi_2O_3 in the reaction⁶. This excess was subsequently removed with a nitric acid leach. The resulting powder was found to be a pure perovskite (rhombohedral angle $89^\circ 30'$, cell edge $3.958 \text{ \AA}$) and was used in the neutron diffraction work.

While a structure for BiFeO_3 was established from the neutron diffraction data, the material had been the subject of so much controversy, and the impurity problems connected with it were sufficiently difficult, that at least partial verification of the structure by an independent method was very desirable. For this reason a program of attempting to grow single crystals of BiFeO_3 was initiated. The program was successful to the extent required for verification of the previous results. One of the first small crystals grown, about 50 microns in size, was used with a very long exposure (1 week) in a Weissenberg camera. A superstructure peak, agreeing with the structure obtained by neutron diffraction, was found, corroborating the doubled (two formula unit) unit cell of BiFeO_3 . A larger crystal, of about 1 mm dimension, was tested for dielectric hysteresis at liquid nitrogen temperature. A hysteresis loop was obtained⁵. The polarization measured was substantially lower than one would expect if the full polarization

of BiFeO_3 was reversed. It is not surprising, however, that there was only partial reversal when one considers that this measurement was made about 1050°C below the dielectric Curie point. The existence of a hysteresis loop confirmed the presence of ferroelectric properties in BiFeO_3 .

Another part of the research concerned the properties of solid solutions of BiFeO_3 - PbTiO_3 - PbZrO_3 ^{7,8}. The PbTiO_3 - PbZrO_3 series itself has been very thoroughly investigated, since it includes the most widely used commercial piezoelectric. On the other hand, data were also available on the BiFeO_3 - PbTiO_3 system^{8,9}, showing that the tetragonal c/a ratio in some of these compositions approached 1.2, a startlingly high value if the strain was associated with ferroelectricity. In analogy with the experience on the system PbTiO_3 - PbZrO_3 , where the combination of a very highly tetragonal material with an antiferroelectric resulted in a piezoelectric of great utility, it seemed desirable to explore the BiFeO_3 - PbTiO_3 - PbZrO_3 system for dielectric properties. This was accomplished. The dielectric measurements on the system, carried out at high frequency (about 1 GHz) and at high temperature (up to 800°C) showed that compositions approaching BiFeO_3 did indeed have very high dielectric Curie points. The Curie point of pure BiFeO_3 could not be determined by direct measurement, because the conductivity of the material is too high, but by extrapolation from the Curie points of solid solutions containing as much as 90 percent BiFeO_3 , the Curie point of the pure material was seen to be in the neighborhood of 850°C . These data were obtained before the structure analysis and showed for the first time that BiFeO_3 was definitely either ferroelectric or antiferroelectric.

The solid solutions of $\text{BiFeO}_3\text{-PbTiO}_3\text{-PbZrO}_3$ do not, however seem to offer the prospect of improved piezoelectric properties as compared with those now available in the $\text{PbTiO}_3\text{-PbZrO}_3$ system, at least for most applications. The higher Curie points obtained in adding BiFeO_3 are offset by increased conductivity and higher electric coercive field, which render the electrical orientation (poling) of piezoelectric ceramics difficult. The increased polarization indicated in solid solutions containing about 70 percent BiFeO_3 and 30 percent PbTiO_3 (high polarization is indicated by the elevated Curie point) may be useful if single crystals of this solid solution can be grown, but the work to date has only shown which compositions are likely to be useful.

The system $\text{BiFeO}_3\text{-PbZrO}_3$ was noticeably different in its behavior from $\text{BiFeO}_3\text{-PbTiO}_3$ ⁸. In making solid solution of two perovskite-type ferroelectrics ABO_3 and A'B'O_3 , one usually finds that the solid solutions have markedly less distinguishable ferroelectric properties than either of the end members, unless A and A' are the same element, as in Pb(Ti, Zr)O_3 , or B and B' are the same, as in $(\text{Ba, Pb})\text{TiO}_3$. In the two cases cited, there is a relatively continuous change of properties from one end of the solid solution series to the other. Surprisingly, this is also true of the series $\text{BiFeO}_3\text{-PbTiO}_3$. It is not true, however, for the series $\text{BiFeO}_3\text{-PbZrO}_3$, in which the compositional region between about 20 and 80 mol percent BiFeO_3 (with Curie points ranging from 150°C to 600°C) has a crystal structure indicative of random deformations from the perovskite structure. In general the addition of PbZrO_3 or PbSnO_3 to solutions of $\text{BiFeO}_3\text{-PbTiO}_3$ tends to "wash out" ferroelectric distortions. It is not clear why Ti is so very

different in its effect from Zr in these compositions, though it is known that the latter has a slightly larger ionic radius and is somewhat less polarizable.

Mössbauer spectrometry was also undertaken on solid solutions of BiFeO_3 - PbTiO_3 - PbZrO_3 ^{10,11}. Here the presence of iron offered the advantage that a Mössbauer isotope having a narrow linewidth was a constituent of the solution. The data obtained offered some intriguing possibilities for the combining of ferroelectric and ferromagnetic properties. For example, it was determined that the extent of magnetic ordering is extremely sensitive to composition of the rhombohedral BiFeO_3 - PbTiO_3 solid solution, near the rhombohedral-tetragonal phase boundary. This suggests that the magnetic properties of this material may be quite sensitive to electric field or to the elastic strain. Again, the effect would be more useful if single crystals were available.

The Mössbauer absorption cross-section was found to decrease in the temperature range around the Curie point in these solutions. This was in agreement with results obtained in other ferroelectrics and is essentially due to the softening of the lattice (soft mode) in this temperature range. One interesting result obtained was that the solid solution $(\text{BiFeO}_3)_{.05}$ - $(\text{PbZrO}_3)_{.95}$, which is antiferroelectric, also shows the same softening effect near its Curie point. In fact, the effect may even be enhanced at the antiferroelectric-cubic transition. Since it is known from dielectric susceptibility data that in a transition to an antiferroelectric, the softening of the mode at $k = 0$ is not as significant as in a ferroelectric (this is shown by the fact that the dielectric constant anomaly at an antiferroelectric Curie point is much less significant than at a ferroelectric Curie

point for the same type of compound), these data bear out qualitatively a suggestion by Dvorak¹² on antiferroelectricity and the Mössbauer effect. His idea was that if the whole transverse optic branch of frequencies becomes low at an antiferroelectric transition, as opposed to only the $k \approx 0$ frequencies at a ferroelectric transition, this should result in a more pronounced Mössbauer anomaly at an antiferroelectric transition. Actually, where inelastic neutron scattering investigations have been possible on ferroelectrics¹³, it appears that the transverse optic mode becomes soft at a transition not only at $k \approx 0$, but over a substantial part of the Brillouin zone in the neighborhood of the origin. A similar effect must occur in antiferroelectrics, as shown by our measurements, but the frequency lowering in the Brillouin zone should be more uniform.

The investigation of the BiFeO_3 - PbTiO_3 - PbZrO_3 system, and the structural similarity between rhombohedral ferroelectric BiFeO_3 and rhombohedral ferroelectric PbTiO_3 - PbZrO_3 , suggested that it would be useful to determine one of the unknown structures in the latter system. This structure was a low temperature phase resulting from a transition originally discovered by Barnett¹⁴ from dielectric considerations. At the time that our work began, no structural explanation was known for this low temperature phase. Our neutron diffraction pattern showed that the low temperature phase had superstructure, and that this superstructure was identical to that of BiFeO_3 ¹⁵. Subsequently, calculation showed that in both materials the superstructure was a result of a tilting the octahedra, formed by the small cation (Fe, Ti, or Zr) and its six nearest-neighbor oxygen atoms, about the $\langle 111 \rangle$ crystallographic axis. Again, a long

exposure of a small single crystal of $\text{Pb}(\text{Ti}, \text{Zr})\text{O}_3$ in a Weissenberg camera showed X-ray superstructure confirming the neutron diffraction results. In BiFeO_3 , the tilting of the octahedra is more pronounced than in $\text{Pb}(\text{Ti}, \text{Zr})\text{O}_3$. The same type of tilting appears in very pronounced form in LiNbO_3 , a ferroelectric with a Curie point of about 1200°C which is widely used in electro-optic technology. The main development of the theoretical and experimental study of this tilting has been in the compounds LaAlO_3 (rotation about $\langle 111 \rangle$) and SrTiO_3 (rotation about $\langle 100 \rangle$)¹⁶. In both of these materials, the tilting angle is small, but comparatively accessible to study. Our work on the extent of the rotation as a function of temperature shows that $\text{Pb}(\text{Ti}, \text{Zr})\text{O}_3$ and LaAlO_3 display the same temperature dependence, even though in the former the rotational transition occurs at a temperature below the ferroelectric transition. This work was also extended to a series of fluorides which show similar behavior^{17,18}.

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Recent Publications

Mössbauer Effect in the Ferroelectric PbTiO_3 - BiFeO_3 Solid Solutions, C. M. Yagnik, J. P. Canner, R. Gerson and W. J. James, J. Appl. Phys., 40, 4713, 1969.

Mössbauer Studies of PbTiO_3 - BiFeO_3 Perovskite-Type Solid Solutions, C. M. Yagnik, R. Gerson and W. J. James. This article has been accepted by the Journal of Applied Physics, but needs to be revised before publication.

Dielectric Hysteresis in Single Crystal BiFeO_3 , James R. Teague, Robert Gerson and W. J. James, Solid State Communications, to be published.

Atomic Displacement Relationship to Rhombohedral Deformation in Some Perovskite-type Compounds, Jean-Michel Moreau, Christian Michel, R. Gerson and W. J. James, Acta Cryst., to be published.

Structural Relationships in Compounds with $R\bar{3}c$ Symmetry, C. Michel, J. M. Moreau and W. J. James, Acta Cryst., to be published.

X-Ray and Neutron Diffraction Study of BiFeO_3 , W. J. James, J. M. Moreau, C. Michel and R. Gerson. To be submitted to the Journal of Physics and Chemistry of Solids.

Degrees Granted

Doctoral degrees in Physics were awarded to the following contract personnel:

James P. Canner (August, 1969)

Christian Michel (all requirements have been completed, and the degree will be awarded in August, 1970)

Personnel

The following personnel were active in this grant during the last contract period.

Project Directors

Robert Gerson, Professor of Physics, University of Missouri - Rolla; 40% time, academic year.

William J. James, Professor of Chemistry and Director, Graduate Center for Materials Research; 20% time, academic year; 25% time, summer.

Other Professional Staff (all paid from grant funds)

Christian Michel, Docteur de Troisieme Cycle, Grenoble, France, 1967. Dr.

Michel's French degree is intermediate between an American M.S. and Ph.D. He will receive the Ph.D. here in August, 1970.

James R. Teague, M.S., New Mexico Highlands University, 1968.

Dr. C. M. Yagnik, Poona University (Ph.D. 1968), post-doctoral fellow.

Roberta A. Lamar, B.S., Alabama College, 1954.

Mrs. Lamar was working as a chemical technician on a half-time basis.

The following were also working on the project, but were not supported by grant funds during the past contract year;

Jean-Michel Moreau, Docteur de Troisieme Cycle, Grenoble, France, 1968.

Dr. Moreau is receiving support from the Graduate Center for Materials Research of the University of Missouri - Rolla, of which Dr. James is Director.