1967

An x-ray study of the lead titanate-bismuth chromate system

Tsen-tsou Shih

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AN X-RAY STUDY OF THE LEAD TITANATE--BISMUTH
CHROMATE SYSTEM

BY
TSEN-TSOU SHIH -1940

A
THESIS
submitted to the faculty of
THE UNIVERSITY OF MISSOURI AT ROLLA
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Approved by

W. J. James (advisor)  

Raymond L. Franklin
ABSTRACT

The lead titanate-bismuth chromate system was studied employing x-ray diffraction techniques at both room and high temperatures. Samples were prepared by sintering stoichiometric mixtures of the corresponding oxides followed by air quenching. Bismuth chromate was prepared by resintering and air quenching for four times. The results of the analyses show the structure of BiCrO$_3$ to be tetragonal with 8 molecules per unit cell. Solid solutions exist over the range 100 to 35 mole percent PbTiO$_3$ of the binary system, although small amounts of other phases are present in some regions.

X-ray data at room temperature indicate the tetragonal perovskite structure exists over the range of 100 to 65 mole percent PbTiO$_3$. From 60 to 35 mole percent PbTiO$_3$ the structure is cubic.

Dielectric measurements show that the specimen containing 95 mole percent PbTiO$_3$ is ferroelectric with a Curie point of 475°C, slightly lower than that of pure PbTiO$_3$. From 90 to 50 mole percent PbTiO$_3$ the samples are too conductive for meaningful dielectric measurements.

High temperature x-ray results show that the Curie point drops almost linearly from 100 to 65 mole percent PbTiO$_3$. The phenomenon is exhibited by ferroelectric binary systems containing PbTiO$_3$ with the exception of the PbTiO$_3$-BiFeO$_3$ system.
ACKNOWLEDGEMENTS

The author wishes to thank Dr. William J. James, Director of the Graduate Center for Materials Research and Professor of Chemistry, and Dr. Robert Gerson, Professor of Physics, for their guidance, support, and encouragement during the course of this investigation. The author is also greatly indebted to Mr. Gary D. Achenbach and Mr. Harlen Rice for their assistance with the high temperature x-ray unit.

The financial assistance of the Atomic Energy Commission in the form of a research fellowship is also gratefully acknowledged.
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I. INTRODUCTION

In 1960, BiFeO$_3$ was reported\(^{(6)}\) to have the perovskite structure. The compound is believed to be ferroelectric \(^{(19)}\) with a Curie point of about 900°C, which is the highest Curie point known. The ionic radius of Cr$^{3+}$, 0.63 Å, is about the same as that of Fe$^{3+}$, 0.64 Å. Therefore a perovskite-type structure might be predicted for BiCrO$_3$. Single phase BiCrO$_3$ was reported\(^{(21)}\) in 1965 to have a triclinic pseudocubic perovskite structure.

The Curie point of pseudo-binary solid solutions of perovskites containing PbTiO$_3$ usually decreases upon substitution of other perovskite components as discussed in Sec. II-C. The sole exception is the PbTiO$_3$-BiFeO$_3$ system. Here the tetragonal distortion from the ideal perovskite structure varies from 1.063 for pure PbTiO$_3$ to 1.17 for 32 weight percent PbTiO$_3$ causing the Curie point to increase as the concentration of BiFeO$_3$ is increased.

The purpose of this investigation was to prepare and study solid solutions of PbTiO$_3$ containing BiCrO$_3$ with regard to crystallographic symmetry and electrical properties. It was of particular interest to see if ferroelectric properties were enhanced upon substitution of BiCrO$_3$, as found in the PbTiO$_3$-BiFeO$_3$ system, or diminished, as observed in other pseudo-binary systems containing PbTiO$_3$. 
II. REVIEW OF LITERATURE

A. Perovskite Ferroelectrics

Crystals lacking a center of symmetry may be piezoelectric. A piezoelectric crystal shows a displacement of electric charge upon an application of external stress. This behavior is exhibited by 20 of the 21 non-centrosymmetric crystal classes. A subgroup of piezoelectrics shows pyroelectricity.\(^{(1)}\) The spontaneous polarization of a pyroelectric crystal is altered with change in temperature. Both piezoelectricity and pyroelectricity are inherent properties of a crystal which require a crystal structure to contain a polar axis along which atomic displacement can take place asymmetrically.

Ferroelectrics are a class of pyroelectrics with the additional property that spontaneous polarization can be reversed by applying a sufficiently intense electric field. The presence of domains* in the ferroelectric crystal produces a hysteresis in the polarization when an alternating field is applied. A typical hysteresis loop for a ferroelectric crystal is shown in Figure 1. The hysteresis disappears at a certain temperature, called the Curie point. The structure undergoes a transition at this temperature from the polar to non-polar state; the high temperature form of the crystal is known as para-

* A part of a twinned crystal which is itself a true single crystal.
Figure 1. Typical hysteresis loop of a ferroelectric crystal.
electric. At the structure transformation, the Curie point, the dielectric constant reaches a maximum. Above this temperature the dielectric constant $\varepsilon$ falls off according to the Curie-Weiss law:

$$\varepsilon - 1 = C/(T-T_c)$$

where

$T_c$ is a temperature close to the Curie point.

$C$ is a constant with the dimensions of temperature.

Among the various types of ferroelectrics, the perovskite family has received much attention following the discovery of ferroelectricity in barium titanate BaTiO$_3$. The general formula of compounds belonging to this family is ABO$_3$, where A is a monovalent, divalent, or trivalent cation and B is a pentavalent, tetravalent, or trivalent cation respectively. The structure of the ideal perovskite can be visualized from Figures 2 and 3 for cubic BaTiO$_3$. The larger cation Ba (or A ion) is located in the center of the cubotetrahedron and has a coordination number 12. The smaller cation Ti (or B ion) is 6 coordinated and is located in the center of the octahedral framework of oxygens. In general, the structure is slightly distorted from the ideal cubic type. Table I lists several perovskite-type compounds. Not all compounds with the formula ABO$_3$, however, have a perovskite-type structure. An important factor that determines the structure type is the geometrical packing of the ions in the lattice. The
Figure 2. Crystal structure of cubic barium titanate. (3)

Figure 3. Crystal structure of barium titanate showing octahedra of oxygen atoms about the titanium atoms. (3)
$C = \text{cubic}; \; T = \text{tetragonal}; \; O = \text{orthorhombic}$. A star in front of the values of the lattice parameters denotes a multiple unit cell. The orthorhombic distortion is described in terms of monoclinic axes. $(F)$ in the last column indicates that the phase transition to the cubic phase coincides with the ferroelectric Curie point.

### TABLE I

<table>
<thead>
<tr>
<th>Compound</th>
<th>Structure at 20 °C</th>
<th>Transition temperature to cubic phase (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Symmetry</td>
<td>Lattice parameters</td>
</tr>
<tr>
<td>BaTiO$_3$</td>
<td>$T$</td>
<td>3.992</td>
</tr>
<tr>
<td>SrTiO$_3$</td>
<td>$C$</td>
<td>3.905</td>
</tr>
<tr>
<td>CaTiO$_3$</td>
<td>$O$</td>
<td>*3.827</td>
</tr>
<tr>
<td>PbTiO$_3$</td>
<td>$T$</td>
<td>3.005</td>
</tr>
<tr>
<td>CdTiO$_3$</td>
<td>$O$</td>
<td>*3.791</td>
</tr>
<tr>
<td>PbZrO$_3$</td>
<td>$O$</td>
<td>*4.159</td>
</tr>
<tr>
<td>PbHfO$_3$</td>
<td>$O$</td>
<td>*4.136</td>
</tr>
<tr>
<td>KNbO$_3$</td>
<td>$O$</td>
<td>4.038</td>
</tr>
<tr>
<td>NaNbO$_3$</td>
<td>$O$</td>
<td>*3.914</td>
</tr>
<tr>
<td>AgNbO$_3$</td>
<td>$O$</td>
<td>*3.944</td>
</tr>
<tr>
<td>KTaO$_3$</td>
<td>$C$</td>
<td>3.989</td>
</tr>
<tr>
<td>NaTaO$_3$</td>
<td>$O$</td>
<td>*3.892</td>
</tr>
<tr>
<td>AgTaO$_3$</td>
<td>$O$</td>
<td>*3.931</td>
</tr>
</tbody>
</table>

Representatives of perovskite-type compounds. (1)
packing of this structure can be related to the ionic radii by the following equation:

\[ R_A + R_O = t \sqrt{2} (R_B + R_O) \]

where

- \( t \) = tolerance factor.
- \( R_A \) = ionic radius of larger cation A.
- \( R_B \) = ionic radius of smaller cation B.
- \( R_O \) = ionic radius of oxygen.

For an ideal perovskite, \( t \) is exactly equal to unity. For perovskites of the type \( A^{2+}B^{4+}O_3 \) and \( A^{3+}B^{3+}O_3 \), the tolerance factor has been assigned a value between 0.99 and 0.77\(^{(4)}\)(\(^{(5)}\)) although exceptions have been reported. Roth\(^{(4)}\) classified perovskites according to the ionic radii of the constituents (Figures 4-7). A three-dimensional graph was also constructed for the perovskite type \( A^{2+}B^{4+}O_3 \) compounds using \( A^{2+} \) and \( B^{4+} \) ions as two coordinates and the polarizability of the \( A^{2+} \) ions as the third coordinate (Figure 6). As very little is known quantitatively about the polarization of the trivalent ions in perovskite \( A^{3+}B^{3+}O_3 \) compounds, this factor has not been used to classify these structures for \( A^{3+}B^{3+}O_3 \). It can be seen from Figure 7 that all the perovskite-type structures occur in the upper left portion of the diagram. No \( A^{3+}B^{3+}O_3 \) compound is known to have a simple cubic perovskite-type structure. As \( Bi^{3+} \) has a radius of 0.96 Å (between \( Y^{3+} \) and \( Sm^{3+} \)), Figure 7 predicts the possibility of BiCrO\(_3\) being
Figure 4. Classification of the perovskite $A^{2+}B^{4+}O_3$-type compounds according to the constituent ionic radii.\(^{(4)}\)

- $\bigcirc$, Compounds studied in the present work that have the structure shown by the areas bounded by dashed lines; $\bullet$, compounds not studied in the present work that are assumed to have the structure shown by the areas bounded by dashed lines; $\ast$, compounds studied in the present work that do not have the perovskite type structure; $X$, position of compositions studied in the present work that do not form $A^{2+}B^{4+}O_3$ compounds.

As the compound CaMnO$_3$ has not been studied in the present work and conflicting reports on its symmetry exist, it is tentatively left on the border between orthorhombic and pseudocubic types and is shown by question mark over symbol.

Figure 5. Graph of ionic radii of $B^{4+}$ ions and polarizability of $A^{2+}$ ions for some of the compounds of the $A^{2+}B^{4+}O_3$ perovskite structure type.\(^{(4)}\)
Position of compounds of the orthorhombic perovskite structure type; \( \Delta \), position of compounds of the cubic or pseudocubic perovskite structure type; \( \Box \), position of compounds having ferroelectric or antiferroelectric perovskite structure types.

Coarse shading indicates boundary between orthorhombic and pseudocubic structure types; medium shading, boundary enclosing compounds of ferroelectric and antiferroelectric structure types; crosshatch shading, boundary between perovskite and SrVO\(_3\) structure types. The boundary between cubic and pseudocubic perovskite types has not been shown on this diagram for the sake of clarity.

Figure 6. Three dimensional graph of the perovskite-type \( \text{A}^{2+}\text{B}^{4+}\text{O}_3 \) compounds using ionic radii of the \( \text{A}^{2+} \) and \( \text{B}^{4+} \) ions as two coordinates and the polarizability of the \( \text{A}^{2+} \) ions as the third coordinate. (4)
0, Rhombohedral perovskite, \( \alpha > 90^\circ \); □, orthorhombic perovskite (CaTiO\(_3\) type); \( \Delta \), Tl\(_2\)O\(_3\) structure type; ◆, corundum structure type; □, La\(_2\)O\(_3\) structure type; ○, compounds not studied in the present work that are not assumed to have the structure shown by the areas bounded by dashed lines.

Figure 7. Classification of the \( \text{A}^{3+}\text{B}^{3+}\text{O}_3\)–type compounds according to the constituent ionic radii.\(^{(4)}\)
a perovskite-type structure of low symmetry. Recently, Filip'ev(6) and Fedulov(7) reported that bismuth ferrate, BiFeO₃, has a rhombohedral distorted perovskite structure. This provides further evidence of the possible existence of perovskitic BiCrO₃, since the ionic radius of Cr³⁺ (0.63 Å) is essentially equal to that of Fe³⁺ (0.64 Å).

B. Lead Titanate, PbTiO₃

Lead titanate has been studied extensively by many investigators. Naray-Szabo(8) first reported the structure to be a tetragonal perovskite with \( a = 3.89 \) Å, and \( c = 4.13 \) Å, one molecule per unit cell. Precise lattice parameters at room temperature were determined in 1951 by Shirane et al(9) with \( a = 3.894 \) Å, and \( c = 4.140 \) Å. The space group is P4mm.

The axial ratio \( c/a \) at room temperature is 1.063, markedly larger than any other perovskite with the same structure. Above room temperature \( c \) decreases and \( a \) increases until just below the transition point, 490°C, \( c/a \) is 1.02. Figures 8-12 show the temperature dependence of the lattice parameters, the axial ratio, the cell volume, specific heat, and dielectric constant respectively.

A further phase transition(12) occurs at approximately -100°C as the crystal is cooled slowly. The low temperature phase appears to be non-ferroelectric and possesses a multiple tetragonal cell. The new dimensions
Figure 8. Lattice parameters as a function of temperature of PbTiO₃. (10)

Figure 9. Axial ratio as a function of temperature of PbTiO₃. (10)
Figure 10. Unit cell volume as a function of temperature of PbTiO$_3$.$^{(10)}$

Figure 11. Specific heat of lead titanate PbTiO$_3$.$^{(9)}$
Figure 12. Variation of permittivity with temperature of PbTiO₃. (11)
are \( a' = 4a, c' = 2c \).

The atomic positions of the room temperature phase of lead titanate were determined in 1956 by Shirane et al.(13) using both x-ray and neutron diffraction. The results are given in Figures 13-15 and Tables II-III. Taking Pb at the origin, both \( O_1 \) (located above and below Ti along the tetragonal axis) and \( O_{II} \) (the other oxygen atoms) are shifted in the same direction by the same amount, 0.47 Å. Ti is shifted by 0.17 Å in the same direction as the three oxygens. The oxygen octahedron remains undistorted. Figure 13 shows the structure of tetragonal \( \text{PbTiO}_3 \) with oxygen defining the lattice. The large shifts of Ti and Pb ions cause the change in bond length. The bond lengths in the cubic structure at 490°C and those of the tetragonal structure at room temperature are given in Table II. Passing from the cubic structure above the Curie temperature to the tetragonal structure, the oxygen octahedron suffers only a uniform elongation due to the tetragonal distortion. The Ti-O\(_1\) bond undergoes a drastic change as can be seen from Figure 14. The Ti-O\(_1(+)\) bond length is 1.78 Å, much shorter than the sum of the Goldschmidt radii which is 1.96 Å. The Pb-O\(_{II}\) length is 2.53 Å, and the Goldschmidt radius is 2.78 Å.

Megaw(2)(14) explained the large axial ratio and high Curie point of \( \text{PbTiO}_3 \) as a consequence of homopolar bond formation by Pb; the tendency of Pb\(^{2+}\) to form unsymmetrical covalent bonds, as is found in tetragonal PbO. Pb
Figure 13. Crystal structure of tetragonal PbTiO$_3$: oxygen octahedron defining the lattice. (13)

Figure 14. Environment of Ti in PbTiO$_3$. (13)

Figure 15. Environment of Pb in PbTiO$_3$. (13)
TABLE II

O\(_{1}(+)\) means the O\(_1\) is close to Ti; O\(_{II}(+)\) is close to Pb

All distances in Ångström units

<table>
<thead>
<tr>
<th>Bond length in tetragonal and cubic PbTiO(_3) structures.(^{(13)})</th>
</tr>
</thead>
</table>

**TABLE II**

<table>
<thead>
<tr>
<th></th>
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<th>Tetragonal</th>
<th>Cubic (at 400(^\circ) C.)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>(\delta_{zT}=+0.040)</td>
<td>(\delta_{zO}=+0.112)</td>
<td>(a)</td>
</tr>
<tr>
<td>Ti-O(_{1}(+))</td>
<td>1.78</td>
<td>2.08</td>
<td>1.98</td>
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<tr>
<td>Ti-O(_{1}(-))</td>
<td>1.88</td>
<td>1.95</td>
<td></td>
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<tr>
<td>Pb-O(_{1})</td>
<td>2.80</td>
<td>2.76</td>
<td>2.80</td>
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<tr>
<td>Pb-O(_{II}(+))</td>
<td>2.83</td>
<td>2.85</td>
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</tr>
<tr>
<td>Pb-O(_{II}(-))</td>
<td>3.20</td>
<td></td>
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Comparison of observed and calculated intensities from neutron diffraction of PbTiO\(_3\).\(^{(13)}\)

**TABLE III**

<table>
<thead>
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<th>First run</th>
<th>Second run</th>
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<td>(I_0-A)</td>
<td>(I_2-A)</td>
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<tr>
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<td>205</td>
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<td>100</td>
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<td>254</td>
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<td>220,003</td>
<td>318</td>
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<td>222</td>
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<tr>
<td>222,300</td>
<td>238</td>
<td>249</td>
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<tr>
<td>103</td>
<td>282</td>
<td>307</td>
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<td>310,301</td>
<td>1230</td>
<td>1307</td>
</tr>
<tr>
<td>113</td>
<td>347</td>
<td>385</td>
</tr>
</tbody>
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lies at the apex of a flat pyramid with a square base containing O's at the corners. The pyramid height is 0.46 Å as compared with 1.16 Å in PbO. This covalent system of Pb-O bonds creates conditions which favor the development of unsymmetrical Ti-O bonds, or the off-centering of Ti in the oxygen octahedron, to produce a polar axis.

C. Solid Solutions of PbTiO₃

Lead titanate has the highest Curie point among the perovskite-type ferroelectrics. Almost any substitution of Pb or Ti with suitable atoms which form a perovskite-type lattice causes a lowering of the Curie point. The systems PbTiO₃-CaTiO₃, PbTiO₃-CaZrO₃, and PbTiO₃-CaSnO₃ were studied in recent years. The crystallographic results are given in Figures 16-18. The phase diagrams of the systems of the lead titanate side were constructed from x-ray phase analysis and the dielectric measurements as shown in Figure 19. It can be seen that the Curie point falls with the increase of the concentration of the second component in all three systems.

Figure 20 shows the dependence of the Curie point upon composition when Pb is replaced by Ba, Sr, or Ca. In three cases the Curie point decreases almost linearly with increasing content of the substituted atoms. The axial ratio c/a of the tetragonal solution at room temperature decreases accordingly. The two lower transition tempera-
Figure 16. Lattice spacing of the PbTiO₃-CaTiO₃ system at room temperature. (16)

Figure 17. Lattice spacing of the PbTiO₃-CaZrO₃ system at room temperature. (17)

Figure 18. Lattice spacing of the PbTiO₃-CaSnO₃ system at room temperature. (17)
Figure 19. Phase diagrams of the PbTiO$_3$ side of the systems (1) PbTiO$_3$-CaTiO$_3$, (2) PbTiO$_3$-CaZrO$_3$, and (3) PbTiO$_3$-CaSnO$_3$.

Figure 20. Phase diagrams of the systems PbTiO$_3$-BaTiO$_3$, PbTiO$_3$-SrTiO$_3$, and PbTiO$_3$-CaTiO$_3$. (2)
tures of BaTiO$_3$, however, decrease with increasing concentration of Pb.

The PbTiO$_3$-BiFeO$_3$ system was investigated by Fedulov. (18) (19) A continuous series of solid solutions was found existing in the entire range of the system. A narrow two phase region was observed from 65-72 weight percent BiFeO$_3$ as seen from Figures 21-23. In the tetragonal phase the lattice parameter $c$ increases sharply with increasing bismuth ferrate whereas $a$ decreases somewhat. The $c/a$ ratio increases from 1.063 for 100 percent PbTiO$_3$ to 1.17 for 68 weight percent BiFeO$_3$. On transferring from the tetragonal modification to the rhombohedral modification, the unit cell volume decreases sharply, $\Delta v = 3.5$ Å$^3$. In the rhombohedral region the parameter $a$ is practically unchanged with increase in BiFeO$_3$ concentration. The rhombohedral angle remains constant. This is the only known system containing PbTiO$_3$ in which the Curie point increases as the concentration of PbTiO$_3$ decreases.

D. Bismuth Chromate, BiCrO$_3$

The earliest report of BiCrO$_3$ was made by Naray-Szabo (8) in 1947. He described the structure of BiCrO$_3$ as a tetragonal perovskite with $a = 7.75$ Å, and $c = 7.95$ Å, with 8 molecules per unit cell. The ceramic sample was prepared by heating a stoichiometric mixture of oxides (nitrates or carbonates) at 700-800°C for 3 hours. Detailed X-ray results of his studies are given in
Figure 21. Change in the lattice constants in a system of solid solutions of PbTiO₃-BiFeO₃ as a function of the composition. (18)

Figure 22. The volume and axial ratio c/a of the unit cells of solid solutions in the PbTiO₃-BiFeO₃ system versus the composition. (18)

Figure 23. Complete phase diagram of the PbTiO₃-BiFeO₃ system. (I) Tetragonal region; (II) tetragonal + rhombohedral region; (III) rhombohedral region. (19)
Appendix C.

In 1954, Keith\(^{(5)}\) reported that it was not possible to confirm the structure reported by Naray Szabo. He stated that the volatility of Bi\(_2\)O\(_3\) made it difficult to obtain solid state reaction.

In 1962, Buhrer\(^{(20)}\) tried to synthesize BiCrO\(_3\) from both oxides and coprecipitated hydroxides. He failed, however, to obtain a single-phase perovskite.

More recently, Sugawara et al.\(^{(21)}\) prepared single phase BiCrO\(_3\) by sintering the mixed oxides at 700°C under a pressure of 40 kbars and then quenching. X-ray diffraction showed it to have a distorted perovskite structure with a triclinic pseudo-cubic unit cell. The lattice parameters were \(a = c = 3.90\ \text{Å}, \ b = 3.87\ \text{Å}, \ a = \gamma = 90°35', \beta = 89°10'\). Sugawara attributed the complicated distorted structure to the covalent character of Bi\(^{3+}\). No further information was reported except that BiCrO\(_3\) was not ferromagnetic down to 77°K.

Venevtsev et al.\(^{(22)}\) studied the effect of the addition of Bi\(_2\)O\(_3\)·Cr\(_2\)O\(_3\) to BaTiO\(_3\). It was found that in the range of small additions, the Curie temperature was not lowered, and for some specimens it was even somewhat higher than that of the initial BaTiO\(_3\). The tetragonal distortion disappeared and the cells of the perovskite phase became cubic at a content of more than 2.6 mole percent BiCrO\(_3\).

Ikeda and Okano\(^{(23)}\) studied the change in the piezoelectric behavior of the PbTiO\(_3\)-PbZrO\(_3\) system upon addition
of BiCrO$_3$. They investigated mainly the rhombohedral-tetragonal phase boundary of the system upon addition of BiCrO$_3$. The width of the investigated region was from 40 to 70 mole percent BiCrO$_3$. The boundary between the tetragonal (F$_t$) and rhombohedral (F$_r$) phases, lies at 55 mole percent PbZrO$_3$, and does not shift with temperature up to the Curie point, 370°C. This boundary shifts to the PbTiO$_3$ side gradually with increasing BiCrO$_3$ substitution. The ferroelectric Curie point was found to decrease with increasing BiCrO$_3$ content.
III. EXPERIMENTAL

A. Materials

The materials used in the preparation of the various samples were PbO, TiO₂, Bi₂O₃, and Cr₂O₃. The purity and manufacturer of each of these oxides are listed in Appendix A.

B. Apparatus

The uses of the various apparatus will be described here, and a list of apparatus is given in Appendix B.

1. Analytical balance. A single pan electric balance was used in weighing the materials to make the samples. The sensitivity of the balance was 1/10,000 gram.

2. Ball mill. A ball mill was used for mixing the samples for sintering. The ball mill was constructed from a 250 ml plastic bottle that contained about 25 ceramic balls of 0.4 inch in diameter and could be rotated at an inclined angle by a variable speed motor.

3. Pill die. A stainless steel die of 3/8 inch diameter was used to press the mixed oxides to form discs for sintering.

4. Crucible. A morganite crucible with a lid, lined with platinum foil, was used to sinter the samples. The crucible was approximately 0.8 inch in diameter and 0.875 inches high.

5. Furnace. Two furnaces were used to sinter the
samples. One was a platinum-wound resistance furnace with a maximum temperature limit of 1300°C. The other was a Kanthal-wound resistance furnace with a maximum temperature of 1000°C. Both furnaces were equipped with automatic controls. Temperatures were accurate to within ±8°C. The furnaces were each calibrated twice to ensure correct temperature.

6. Mortar and pestle. An agate and a porcelain mortar and pestles were employed to grind the sintered sample in preparation for x-ray diffraction analysis.

7. X-ray diffractometer. A Siemens diffraction unit was used for crystallographic analysis. Ni filtered CuKα radiation, \( \lambda = 1.542 \) Å was used.

8. High temperature, high vacuum attachment. The high temperature unit was employed to determine the Curie points of the samples in the system. The maximum temperature of the unit was 1300°C. The vacuum was below 10⁻⁴ torr. A tantalum heating element with the dimensions 3/16" x 5/16" was used as both sample holder and heating stage. Figures 24 and 25 show the construction of the high temperature attachment and the high vacuum system.

C. Preparation of Samples

The compositions were arbitrarily selected at 5 or 10 mole percent intervals between 100 percent lead titanate and 100 percent bismuth chromate. Stoichiometric amounts of materials were weighed to an accuracy of 1/10,000 grams.
Figure 24. Siemens high temperature x-ray diffractometer.

Figure 25. Siemens high temperature x-ray diffractometer and high vacuum system.
The materials were mixed in a ball mill. Distilled water was added to form a slurry. After rotating the sample for 4-5 hours, the slurry was filtered with distilled water and then dried in a drying oven. Samples were then ground, by hand, to a fine powder (approximately 300 mesh) and pressed into discs 3/8 inch in diameter and 1/8 to 3/8 inches in height. The pressure applied was 50,000 psi in most cases.

D. Sintering Procedure

The discs were placed in a platinum-lined morganite crucible with a stainless steel spatula. The covered crucible was put into a preheated furnace. After a temperature recovery period of about 10 minutes, the sample was usually sintered for 2 hours under one atmosphere pressure. After the reaction period, the crucible was removed from the furnace and air quenched. The discs shrank only slightly because of the high pressure applied before sintering. As the sintering temperatures used in this system were generally above 900°C, incomplete reactions on the surface of the discs were evident due to the volatility of PbO and Bi$_2$O$_3$. The outer parts of the discs were removed using a sheet of abrasive paper. The sample was ground by hand with a mortar and pestle to a fine powder of approximately 300 mesh. The sample was then used for x-ray diffraction studies.

For compositions of 40 mole percent PbTiO$_3$ to BiCrO$_3$
resintering techniques were employed in an attempt to obtain complete reaction. This was accomplished by repeating the procedures stated in the last paragraph, that is; regrind, repress, and resinter.

For 100 percent BiCrO$_3$ the sample was preheated at a temperature of 400°C for 1-2 hours. The temperature was then increased and sintering continued for about the same period of time. Sintering under an oxygen atmosphere was also carried out. The sintering temperatures and the other conditions during sample preparation are listed in Appendix D.

E. X-ray Diffraction Analysis at Room Temperature

X-ray diffraction patterns were made of each sintered sample. The samples were mounted on the center of a 3/2" square glass plate. A minute quantity of vaseline was spread on the glass for adhesion of the powdered sample. The surface of the sample was made flat by pressing it against another glass plate. A scanning speed of 1°/min and a chart paper speed of 1 cm/min were generally used. A slower speed of 0.25°/min and a chart paper speed of 2.5 cm/min were used to increase the resolution of certain reflections. An entrance slit of 1 mm and an exit slit width of 0.1 mm were used. The x-ray unit was aligned frequently and provided very good resolution for $K\alpha_1$ and $K\alpha_2$, especially for the high angle reflections.
The lattice parameters were determined from the x-ray patterns. The "d" values for all possible values of "hkl" were calculated using the digital IBM-360-40 computer located on the U.M.R. campus. The volume of the unit cells was determined from the following equations.

\[
V = a^2c \quad \text{Tetragonal}
\]

\[
V = a^3 \quad \text{Cubic}
\]

F. High Temperature Techniques

The Curie point of each specimen was determined using a high temperature x-ray diffractometer. A tantalum, instead of platinum, sample holder was used because tantalum has a very simple structure and d-spacings which are quite different from those of the perovskites. The reflections contributed by the tantalum stage did not superimpose upon those of the perovskites. Since tantalum reacts readily with oxygen and nitrogen at moderate temperatures, it was necessary to use a vacuum of the order of \(10^{-4}\) torr. This was accomplished by using a forepump and a diffusion pump.

The procedure for determining the phase transformation, ferroelectric \(\rightarrow\) paraelectric, was as follows:

A fine powder sample, mixed with drops of ether to form a slurry, was mounted on the surface of the Ta heating element with a stainless steel spatula. The amount of the sample was just enough to form a thin layer. The surface of the sample was made as even as possible. The
heating element was then fixed in place. Alignment was made according to the procedures listed in the Manual.*(24) The vacuum pump system was connected to the high temperature attachment and the system evacuated to the desired pressure.

To obtain the best resolution, a scanning rate of 0.25°/min and a chart paper speed of 2.5cm/min were chosen. An entrance slit of 1mm and an exit slit of 0.2mm were used to obtain reasonably high intensities. The temperature was measured with a chromel-alumel thermocouple, attached to the back of the Ta element, and a portable millivolt potentiometer.

When a vacuum of $10^{-4}$ torr was reached, the x-ray diffraction pattern of a particular pair of reflections was recorded. In this series of samples studied, the pair of reflections (200) and (002) was selected because these peaks possess the maximum splitting among the sets of reflections with strong intensities in the room temperature x-ray pattern.†

* For an unknown reason the correct reflection angles could not be obtained. Therefore a correction of the true angles was made with true angles obtained from the room temperature stage as a standard.

† The (100) and (001) reflections had stronger intensities but their separation was less. The same was true for (110) and (011). (211) and (112) had nearly the same peak separation as (200) and (002) but the intensities were too low for good resolution.
Starting at room temperature, x-ray patterns for various temperatures were obtained. The temperature interval varied from 100°C at temperatures far below the Curie point to within 10°C in the vicinity of the Curie point. X-ray patterns of temperatures above the Curie point up to 700°C were obtained. The equilibrium temperature of each setting could be attained within 10 minutes. A slight fluctuation of the temperature (±2°C) during the measurements was observed occasionally.

For a few samples, x-ray patterns of 2θ range 15-60 degrees at room temperature were made. The relative intensities and the sharpness differed from those patterns obtained with a room temperature stage. The low angle reflection intensities were lower and the high angle reflection intensities were higher; all the peaks were broader. These were the consequences of the uneven surface of the sample on the Ta stage and the smaller amount of sample mounted on the sample holder. A complete x-ray pattern, from 15-60 degrees of 2θ, was made of the 90 percent PbTiO₃ composition at a temperature just above the Curie point. Only lines belonging to a simple cubic pattern of the high temperature phase of the sample were evident as well as several peaks of the Ta stage.

The tetragonal and cubic lattice parameters, c and a, were calculated for each temperature from x-ray data obtained at the various temperatures. A typical plot of the lattice parameters versus temperature is shown in Figure
26. The Curie point was determined from the intersection of the lattice parameters of tetragonal and cubic regions. The x-ray data are given in Appendix F.
Figure 26. A typical plot of the lattice parameters versus temperature for PbTiO$_3$-BiCrO$_3$ system.
IV. RESULTS AND DISCUSSION

A. Sintering

The determination of the time and the temperature for sintering the mixed oxides was a trial and error process. Bismuth chromate was made by repetitive sintering at 800, 850, 900, and 950°C for a period of 2 hours in each sintering. Resintering techniques were required because the higher temperatures necessary to provide sufficient reaction caused some Bi$_2$O$_3$ to melt in the mixture. A temperature of 1000 to 1050°C and a period of 2 hours were used for samples on the PbTiO$_3$ side of the system. Higher sintering temperatures were required to obtain complete solid state reactions as the concentration of BiCrO$_3$ was increased. For example, sintering at 950°C for 95 mole percent PbTiO$_3$ sample gave complete reaction, whereas sintering at the same temperature for 50 mole percent PbTiO$_3$ gave incomplete reaction. For samples from 45 mole percent PbTiO$_3$ to 100 percent BiCrO$_3$ temperatures between 800 and 1200°C were employed. Resintering and multiple-stage sintering were also carried out in an attempt to go to higher temperature without melting the samples. In several cases, the sample fused.

Each sample was pressed into a disc before sintering, in part to shorten the diffusion path length and to prevent the vaporization of low melting point oxides.
losses during sintering were found to be negligible except for those samples sintered at temperatures higher than 1100°C in which case the discs were found to be nonhomogeneous after sintering. Therefore, a closed system would be required for high temperature sintering.

The color of PbTiO₃ is brown. As the BiCrO₃ content is increased in samples of the PbTiO₃-BiCrO₃ system, the color of the powders changes gradually to dark green. The hardness of the sintered discs generally increases as the BiCrO₃ composition is increased.

B. Crystallographic Results at Room Temperature

Pure PbTiO₃ was prepared by sintering equimolar mixtures of PbO and TiO₂ at 1000°C. X-ray results were in good accordance with Shirane's lattice constants and indexing for pure PbTiO₃ as given in Appendix E. The method for preparing bismuth chromate was described in the previous section. X-ray diffraction patterns showed primarily a single phase with a perovskite tetragonal structure. The lattice parameters are a = 7.955 Å, c = 7.902 Å. The pattern is similar to that of Naray-Szabo's except for a few extraneous peaks. Peaks at d = 3.56, 2.64, 2.46, and 1.67 Å, corresponding to the positions of Cr₂O₃ are evident, but strangely there is no evidence of Bi₂O₃ in the x-ray spectra. Weight losses were too small to account for the absence of Bi₂O₃ as resulting from evaporative loss. Attempts to index x-ray data by using
Sugawara's triclinic lattice constants were unsuccessful. Further studies of BiCrO$_3$ are necessary and it is probable that high pressure techniques will be required to prepare single phase material.

In the PbTiO$_3$-BiCrO$_3$ system, single phase solid solutions were prepared over the range 100 to 50 mole percent PbTiO$_3$. From 100 to about 60 mole percent PbTiO$_3$ the structure is tetragonal. The lattice parameter $c$ decreases sharply and $a$ increases gradually with increasing concentration of BiCrO$_3$ (Figure 27). The $c/a$ ratio (Figure 28) decreases from 1.064 for pure PbTiO$_3$ to 1.008 for 65 mole percent PbTiO$_3$. The volume of the unit cell (Figure 28) decreases as the BiCrO$_3$ content is increased. Between 60 to 50 mole percent PbTiO$_3$ the structure is apparently cubic. Below 45 mole percent PbTiO$_3$, x-ray results show multiple phases with a predominance of cubic phase up to 35 mole percent PbTiO$_3$. Some Cr$_2$O$_3$ peaks appear at this composition. Below 30 mole percent PbTiO$_3$, the x-ray patterns were too poor to be analyzed. Further studies in the region below 45 mole percent PbTiO$_3$ are required. The application of high pressure during sintering may be helpful.

C. High Temperature X-ray Analysis

The Curie points of ferroelectric materials are generally determined from dielectric constant measurements. It was not possible to do so for the solid
Figure 27. Lattice parameters of the PbTiO₃-BiCrO₃ system.
Figure 28. Variation of the volume of the unit cell and c/a ratio of the PbTiO₃-BiCrO₃ system.
solutions of this system. The samples were too conductive, no doubt as a consequence of electron hopping, to give sharp peaks in the dielectric constant vs. temperature plot. The room temperature resistivity varies from about $10^8$ ohm-cm for 10 mole percent BiCrO$_3$ to $10^6$ ohm-cm for 40 mole percent BiCrO$_3$, as measured by Mr. James Canner of the physics department. The Curie point of only a 95 mole percent PbTiO$_3$ sample could be determined from dielectric measurements and it was found to be 475°C.

It was therefore necessary to obtain the Curie points of the solid solutions from 95 to 65 mole percent PbTiO$_3$ by high temperature x-ray techniques. The results are given in Table IV and illustrated in Figure 29. The Curie point of the 95 mole percent PbTiO$_3$ sample determined by this method is 465°C, in reasonable agreement with that obtained from the dielectric measurement. Several samples were measured twice. The average deviation between measurements was ± 10°C. Possible errors that can occur in high temperature x-ray diffraction techniques are as follows: First, the thermocouple is attached to the back of the sample holder; therefore, the temperature registered might differ from that of the sample itself. Second, the surface of the sample is rough, causing some local variation in temperature from point to point. Third, the thickness of the sample mounted on the sample holder is difficult to reproduce from measurement to measurement, making it difficult to assure temperature reproducibility.
### TABLE IV

X-ray data on the PbTiO$_3$-BiCrO$_3$ system

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Mole% PbTiO$_3$</th>
<th>Parameters</th>
<th>Volume of Unit Cell (Å$^3$)</th>
<th>c/a</th>
<th>Curie Pt. (°C)</th>
<th>Phases Present</th>
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<td>1-A</td>
<td>100</td>
<td>3.888 4.137</td>
<td>62.556</td>
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<td>490</td>
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<td>3.924 60.421</td>
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<td>cubic</td>
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<td>12-A</td>
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<td>Tetragonal and Cr$_2$O$_3$</td>
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</tbody>
</table>

† Determined from dielectric measurement by James Canner in the Physics Department.
* The other phase is not yet identified unambiguously, possibly the tetragonal BiCrO$_3$ structure.
Figure 29. Curie points of the PbTiO₃-BiCrO₃ system.
It is seen from Figure 29 that the Curie point drops almost linearly as the concentration of BiCrO$_3$ is increased. This is consistent with the crystallographic results at room temperature; one would expect in the simplest case that the less the distortion from the ideal cubic perovskite, the lower the Curie point. The crystal structure of 60 to 50 mole percent PbTiO$_3$ is cubic at room temperature. A Curie point below room temperature is possible. Therefore low temperature x-ray studies are necessary in order to construct the complete phase diagram of the single phase solid solution region of the system. Inasmuch as PbTiO$_3$ is reported to have a low phase transition at -100°C, low temperature x-ray studies over the single phase solid solution region would be of interest.

It is worth noting that as in other pseudo-binary systems, PbTiO$_3$ has an extraordinary capability for bringing BiCrO$_3$ into its perovskitic lattice. The similarity of Cr$^{3+}$ to Fe$^{3+}$ might lead one to expect the behavior of the PbTiO$_3$-BiCrO$_3$ to approximate that of PbTiO$_3$-BiFeO$_3$. Such is not the case, and these results clearly show that ionic size of the ferroactive ion is not a unique factor in determining the tendency to form perovskitic structures of similar properties.
V. BIBLIOGRAPHY


APPENDICES

A. Materials

B. Apparatus

C. X-ray Data for PbTiO₃ and BiCrO₃

D. Sintering Data

E. X-ray Diffraction Data for the PbTiO₃-BiCrO₃ System

F. High Temperature X-ray Diffraction Data for the PbTiO₃-BiCrO₃ System
APPENDIX A

Materials

The following is a list of the materials used in this investigation.

1. Lead oxide (PbO). Laboratory chemical grade (monoyellow), Fisher Scientific Company, Fairlawn, N. J.


APPENDIX B

Apparatus

The following is a list of the apparatus used in this investigation.

1. **Analytical balance.** Sartorius (multi-purpose), Type 2403 (single-pan), 0-100 gm, Aloe Scientific Company, St. Louis, Missouri.


4. **Ball mill, variable speed.** Located in Graduate Center for Materials Research, University of Missouri at Rolla.

5. **Crucible, recrystallized alumina.** Type N4429, Morgan Refractories, England.

6. **Platinum foil, high purity.** 0.001 inch thickness, A. D. Mackey, Inc., New York, N. Y.

7. **Furnace, electrical.** Platinum-wound resistance, located in Chemical Engineering building, University of Missouri at Rolla.

8. **Furnace, electrical.** Kanthal-wound resistance, located in Graduate Center for Materials Research, University of Missouri at Rolla.

9. **X-ray Diffractometer.** Siemens Crystalloflex IV,
Type U13, Siemens America, Inc., Long Island, N. Y.

APPENDIX C

X-ray Data for PbTiO₃ and BiCrO₃

A. Tetragonal PbTiO₃*

Parameters:  $a = 3.905 \text{ Å}, c = 4.151 \text{ Å}.$

<table>
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<tr>
<th>$d$ (Å)</th>
<th>$I/I_0$</th>
<th>$hkl$</th>
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<tbody>
<tr>
<td>4.150</td>
<td>26</td>
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* Taken from ASTM card number 6-0452.

B. Tetragonal BiCrO₃**

Parameters: \(a = 7.75\ \text{Å}, c = 7.95\ \text{Å}\).

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** Reported by Naray-Szabo\(^{(8)}\) at room temperature for CuK\(\alpha\) radiation.
## APPENDIX D

### Sintering Data

#### A. Sintering Data for Samples of the PbTiO\(_3\)-BiCrO\(_3\) System

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Composition (mole%PbTiO(_3))</th>
<th>Pressure* (psi)</th>
<th>Time (hrs)</th>
<th>Temperature (°C)</th>
<th>Sintering System</th>
<th>Quenching</th>
<th>Phases†</th>
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*Pressure refers to the pressure applied during sintering.
†Phases refer to the crystal phases present in the sample.
**Remarks indicate additional notes or conditions that were applied during the experiment.
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<th>Phases† Remarks**</th>
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* Pressure applied before sintering.
† S means single phase; M means multiple phases.
** R means resinter.

B. Sintering Data for the BiCrO₃ Samples

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* Pressure applied before sintering.
† S means single phase; M means multiple phases.
** R means resinter.
### B. (Cont'd)

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†† This sample was inserted in the tube and heated to 800°C and sintered.

* † ** See page 54.
APPENDIX E

X-ray Diffraction Data for the PbTiO₃-BiCrO₃ System

Notes: 1. All x-ray patterns are based on CuKα radiation with a wavelength of 1.542 Å.

2. The indices of the x-ray patterns of each composition include only the main phase (see Table III); the structure is indicated in each table.

3. For the tetragonal patterns, expect BiCrO₃, the parameters a and c were calculated from the 200 and 002 lines, respectively. For BiCrO₃ c was calculated from the 004 reflection and a was calculated from 211, 112, 202, and 220 lines.

4. In the cubic region, the parameter a was determined from the 200 line.

5. The samples used here for each composition are the same as given in Table IV.
a. 100% PbTiO₃

Structure: Tetragonal
Parameters: \( a = 3.888 \text{ Å}, \ c = 4.137 \text{ Å}. \)

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b. 95% PbTiO₃-5% BiCrO₃

Structure: Tetragonal
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c. 90% PbTiO₃-10% BiCrO₃

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d. 85% PbTiO₃-15% BiCrO₃

Structure: Tetragonal
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e. 80% PbTiO₃-20% BiCrO₃

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f. 75% PbTiO₃ - 25% BiCrO₃

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g. 70% PbTiO₃ - 30% BiCrO₃

Structure: Tetragonal
Parameters: $a = 3.911$ Å, $c = 3.961$ Å.

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h. 65% PbTiO₃-35% BiCrO₃

Structure: Tetragonal
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<td>1.604</td>
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<td>1.136</td>
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<td>1.051</td>
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i. 60% PbTiO$_3$-40% BiCrO$_3$

Structure: Cubic
Parameter: $a = 3.926$ Å.

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<td>39.71</td>
<td>2.268</td>
<td>22</td>
<td>111</td>
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<tr>
<td>46.21</td>
<td>1.963</td>
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<td>200</td>
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<tr>
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<td>1.756</td>
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<td>120</td>
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<tr>
<td>57.37</td>
<td>1.605</td>
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<td>211</td>
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<td>67.32</td>
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<td>76.54</td>
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<td>103</td>
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<td>85.40</td>
<td>1.136</td>
<td>1</td>
<td>222</td>
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<td>1.052</td>
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<td>231</td>
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j. 55% PbTiO$_3$-45% BiCrO$_3$

Structure: Cubic
Parameter: $a = 3.925$ Å.

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k. 50% PbTiO$_3$-50% BiCrO$_3$

Structure: Cubic
Parameter: $a = 3.924$ Å.

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1. 45% PbTiO₃-55% BiCrO₃

Structure: Cubic
Parameter: a = 3.924 Å.

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m. 40% PbTiO₃-60% BiCrO₃

Structure: Cubic
Parameter: a = 3.920 Å.

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n. 35% PbTiO₃ - 65% BiCrO₃

Structure: Cubic
Parameter: $a = 3.922 \text{ Å}$.

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o. 100% BiCrO₃

Structure: Tetragonal
Parameters: $a = 7.855 \text{ Å}$, $c = 7.902 \text{ Å}$.

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APPENDIX F

High Temperature X-ray Diffraction Data
for the PbTiO$_3$-BiCrO$_3$ System

a. 95% PbTiO$_3$-5% BiCrO$_3$

Curie point: 465°C.

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<th>c (Å)</th>
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b. 90% PbTiO$_3$-10% BiCrO$_3$

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e. 80% PbTiO<sub>3</sub> - 20% BiCrO<sub>3</sub>
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h. 70% PbTiO$_3$ - 30% BiCrO$_3$

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i. 70% PbTiO$_3$ - 30% BiCrO$_3$

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VITA

Tsen-tsou Shih was born in Kiangsu, China, on January 28, 1940. He graduated from Chiang-Kuo High School in June 1958. He enrolled in the Chung-Hsing University, Taichung, Taiwan, China, in September 1958, and received the Bachelor of Science degree in Chemistry in June 1962.

He worked in the Chemistry Department, Chung-Hsing University as a full time teaching assistant during the period of August 1963 to February 1964.

He entered the Graduate School of the University of Missouri at Rolla in September 1964. From September 1965 to April 1967, he was appointed a research assistant in the Graduate Center for Materials Research of the Space Science Research Center with funds provided by the U. S. Atomic Energy Commission.