Bismuthates: BaBiO$_3$ and related superconducting phases

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Abstract

BaBiO$_3$ has the perovskite structure, but tilting of the BiO$_6$ octahedra destroy the ideal cubic symmetry except at temperatures above 820 K. BaBiO$_3$ is a diamagnetic semiconductor due to a charge density wave (CDW), which is equivalent to a Ba$_2$Bi$^{3+}$Bi$^{5+}$O$_6$ representation. Recent calculations and experimental results confirm that there is no significant deviation from the oxidation states of 3+ and 5+. Superconductivity with a $T_c$ as high as 13 K occurs for BaPb$_{1-x}$Bi$_x$O$_3$ phases where the 6s band is about 25% filled, and superconductivity with a $T_c$ as high as 34 K occurs for Ba$_{1-x}$K$_x$BiO$_3$ phases where the 6s band is about 35% filled. Structures in these two solid solutions can have cubic, tetragonal, orthorhombic, or monoclinic symmetry. However, superconductivity has only been observed when the symmetry is tetragonal.

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1. BaBiO$_3$

1.1. History

BaBiO$_3$ was first prepared in 1963 [1]. Although structure of BaBiO$_3$ was immediately identified as perovskite type, various groups assigned its symmetry as rhombohedral, orthorhombic, monoclinic or triclinic. All groups agreed that that X-ray diffraction showed no evidence of a unit cell larger than that expected for one formula unit of BaBiO$_3$ per unit cell. This indicates an oxidation state of 4+ for Bi because disproportionation of Bi$^{4+}$ into a mixture of Bi$^{3+}$ and Bi$^{5+}$ should produce a larger unit cell. Nonetheless, many investigators assumed that this compound contained a mixture of Bi$^{3+}$ and Bi$^{5+}$ simply because an oxidation state of 4+ for Bi had never been established in any other compound. This

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samples were grown. 5+–O distance in Ba2+ ceramics were not found higher than any was finally resolved in 1976 when a neutron diffraction structure given in Table 1 are based on neutron 1995 [16] is 2.12 Å. Thus, we must con- octahedron had an average Bi–O distance of 2.13 Å [10].

because C forms four single first is then Ba2+ of 13 K in the system BaPb1–x, as well as the assignment of an oxida- tion state of 4+, but 3+–O and Bi3+–O distances found by neutron diffraction. This assignment is based on the dif-

this system, they used the term oxidation state because oxygen was used as the reference. The terms oxidation state and valent state are frequently used interchangeably, but this is not always correct. For example, the oxidation state of V in VO2 is 4+, but the valent state of V is 5. This is because homopolar bonds are ignored in the oxidation state system but not in the valent state system. It is the single bond between two V atoms that brings the V valent state up to 5 in VO2. The valent state and the oxidation state systems are the same when no homopolar bonding is present. In neither the valent state system nor the oxidation state system are the assignments directly related to charges on atoms.

Bonding distances are commonly used to determine the oxidation state of a cation. There are two approaches for using bond distances in this way. One is the use of radii, which vary according to coordination number of the cation and anion as well as other factors. The other approach is the bond valence method, which has largely supplanted the radii approach. Both methods are strictly empirical, and their reliability depends on the quality of the structural data available to implement these methods. At the time when BaBiO3 became of great interest, neither the radii nor the bond valence method were reliable methods for assessing the oxidation states of Bi5+ and Bi3+ in BaBiO3, due primarily to the lack of an adequate database. The methods were used despite this, leading to some erroneous conclusions.

At the time when superconductivity was discovered in BaBiO3 related compounds, very few compounds containing Bi5+ were known and there was no example of a well characterized compound containing a mixture of Bi5+ and Bi3+. The structure of only one Bi5+ containing compound was considered sufficiently established to give reliable Bi–O distances. This was Na3BiO4 where the BiO4 tetrahedron had an average Bi–O distance of 2.13 Å [10]. Today, we have reliable bonding distances for Bi5+ in nine more oxides (Table 2) [11–16]. In all cases, the oxidation state of Bi is well established by the stoichiometry of the compound. Also in all cases, Bi3+ is in a slightly distorted octahedron as in the case of Ba2Bi5+Bi3+O9. We also have bonding distances in Bi5+Bi3+ first prepared in 1995 [12]. Based on the distances given in Table 1, we see that the average of Bi5+–O distances within a BiO4 octahedron can range from 2.09 to 2.13 Å. The five refinements of the Ba2Bi5+Bi3+O9 structure given in Table 1 are based on neutron diffraction using polycrystalline samples [6,8,17–19]. The average Bi5+–O distance obtained by neutron diffraction for the five different determinations of Ba2Bi5+Bi3+O9 is 2.12 Å. Thus, we must consider the Bi5+–O distance in Ba2Bi5+Bi3+O9 to be completely

<table>
<thead>
<tr>
<th>Compound</th>
<th>Average Bi5+–O distance (Å)</th>
<th>Year of structure determination</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na3BiO4</td>
<td>2.130</td>
<td>1972 [10]</td>
</tr>
<tr>
<td>Bi5+Bi3+O9</td>
<td>2.101</td>
<td>1995 [12]</td>
</tr>
<tr>
<td>MgBi2O5</td>
<td>2.097</td>
<td>1997 [13]</td>
</tr>
<tr>
<td>LiBiO3</td>
<td>2.112</td>
<td>1996 [14]</td>
</tr>
<tr>
<td>AgBiO3</td>
<td>2.118</td>
<td>2000 [15]</td>
</tr>
<tr>
<td>NaBiO2</td>
<td>2.116</td>
<td>2000 [15]</td>
</tr>
<tr>
<td>Ba2Bi5+Bi3+O9</td>
<td>2.110</td>
<td>1995 [16]</td>
</tr>
<tr>
<td>Ba2Nd3+Bi5+O6</td>
<td>2.093</td>
<td>1995 [16]</td>
</tr>
<tr>
<td>Ba2Pr3+Bi5+O6</td>
<td>2.092</td>
<td>1995 [16]</td>
</tr>
<tr>
<td>Ba2Bi5+Bi3+O6</td>
<td>2.000</td>
<td>1995 [16]</td>
</tr>
<tr>
<td>Average</td>
<td>2.107</td>
<td></td>
</tr>
<tr>
<td>Ba2Bi5+Bi3+O6</td>
<td>2.120</td>
<td>1976 [6]</td>
</tr>
<tr>
<td>Ba2Bi5+Bi3+O6</td>
<td>2.140</td>
<td>1978 [17]</td>
</tr>
<tr>
<td>Ba2Bi5+Bi3+O6</td>
<td>2.097</td>
<td>1979 [8]</td>
</tr>
<tr>
<td>Ba2Bi5+Bi3+O6</td>
<td>2.116</td>
<td>1990 [18]</td>
</tr>
<tr>
<td>Ba2Bi5+Bi3+O6</td>
<td>2.111</td>
<td>2006 [19]</td>
</tr>
<tr>
<td>Average</td>
<td>2.117</td>
<td></td>
</tr>
</tbody>
</table>

1.2. Oxidation states

Much confusion has existed over the assignment of the oxidation states in Ba2Bi5+Bi3+O9, as well as the assignment of an oxidation state of 3+ to Cu in the cuprate superconductors. Oxidation state assignments in general have no direct relationship with actual charges on cations, except in the case of bonds that are 100% ionic [9]. This system started with organic compounds with very covalent bonds. Here the term valent states is used. Carbon is tetravalent in diamond and in CO2 because C forms four single bonds in diamond and two double bonds to O in CO2. There is no implication of charges on atoms. When inorganic chemists adopted

<table>
<thead>
<tr>
<th>Defect NaCl structure</th>
<th>Highest Tc, (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO, VO, NbO</td>
<td>~1.5</td>
</tr>
<tr>
<td>“Tungsten bronze type” hexagonal and tetragonal</td>
<td>~6</td>
</tr>
<tr>
<td>A,Mo6: M = W, Mo, Re</td>
<td>A = Cu, Na, Nb, Cl, Ca</td>
</tr>
<tr>
<td>Sr, Ba, Tl, In, Nh4</td>
<td></td>
</tr>
<tr>
<td>Li0.9Mo6O17</td>
<td>~2</td>
</tr>
<tr>
<td>Li0.45NbO2</td>
<td>5.5</td>
</tr>
<tr>
<td>Li2FeAsO4</td>
<td>~6</td>
</tr>
<tr>
<td>Ag2O3: X = NO3, HF2, ClO4, BF4</td>
<td>~1.5</td>
</tr>
<tr>
<td>Spinel structure</td>
<td>~14</td>
</tr>
<tr>
<td>LiTi2O4</td>
<td></td>
</tr>
<tr>
<td>Perovskite related</td>
<td>~0.5</td>
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<tr>
<td>SrTiO3</td>
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</tr>
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<td>Sr2BaO4</td>
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<tr>
<td>Pyrochlore structure</td>
<td>~1</td>
</tr>
<tr>
<td>Cd3Be2O7</td>
<td>~9</td>
</tr>
<tr>
<td>Al2O2: A = K, Rb, Cs</td>
<td>~20</td>
</tr>
<tr>
<td>LaFeAsO4 type</td>
<td>134</td>
</tr>
</tbody>
</table>
normal based on current information, which is now extensive. Evaluating of Bi$^{3+}$–O distances is more difficult because the usual coordination of Bi$^{3+}$ in oxides is a highly distorted polyhedron, typical of an $s^2$ cation. Neither the radii nor the bond valence approach cope well with this situation. The coordination of Bi$^{3+}$ in the octahedral site of the perovskite structure is unique in that it is a nearly ideal octahedron. There are apparently no other known case in oxides where Bi$^{3+}$ is at an inversion center. However, we have two compounds with the same structure as Ba$_2$Bi$^{2+}$Bi$^{5+}$O$_6$; Ba$_2$Bi$^{2+}$Sn$^{5+}$O$_6$ and Ba$_2$Bi$^{2+}$Ta$^{5+}$O$_6$  [17,19,20]. Again the oxidation state of Bi is these two cases is well established by the stoichiometry of the compound. The average reported Bi$^{3+}$–O distance from neutron diffraction data for Ba$_2$Bi$^{2+}$Sn$^{5+}$O$_6$ and Ba$_2$Bi$^{2+}$Ta$^{5+}$O$_6$ ranges from 2.28 to 2.31 Å, and the average of reported values for Bi$^{3+}$ in Ba$_2$Bi$^{2+}$Bi$^{5+}$O$_6$ is 2.29 Å. The conclusion then is that Bi$^{2+}$–O and Bi$^{5+}$–O distances in Ba$_2$Bi$^{2+}$Bi$^{5+}$O$_6$ show no deviation from that expected for these assigned oxidation states. A rigorous definition for oxidation states has recently been developed based on wavefunction topology and modern polarization theory  [21]. These calculations also fully support the oxidation state values indicated by the Ba$_2$Bi$^{2+}$Bi$^{5+}$O$_6$ formula, which is equally well described as a charge density wave (CDW).

It is relevant to contrast the CDW in BaBiO$_3$ with that in CaFeO$_3$, which also has the perovskite structure. In the case of CaFeO$_3$, there is no problem applying the radii or the bond valence method to address oxidation state of Fe because of the great abundance of reliable information on Fe–O bond distances with different Fe oxidation states. At 15 K perovskite CaFeO$_3$ has two Fe sites with distinctly different Fe–O bond distances, 1.872 and 1.974 Å  [22]. The Fe on these two sites is sometimes referred to as Fe$^{3+}$ and Fe$^{5+}$, but here the Fe–O bond distances are not consistent with assigning those oxidation states. Bond valence calculations give Fe oxidation state values of 3.48 and 4.58  [22]. These are significantly different from the values expected for Fe$^{3+}$ and Fe$^{5+}$. Thus, the CDW is definitely weaker than that indicated by a formula of Ca$_2$Fe$^{3+}$Fe$^{5+}$O$_6$. Thus, we would expect that this CDW would further decrease in magnitude with increasing temperature, and it does so, disappearing at about 270 K to give metallic CaFe$^{4+}$O$_3$.

1.3. Skipped oxidation states, disproportionation, and negative U

For certain elements, cations with the 6$s^0$ or 5$s^0$ state is well known and the 6$s^5$ or 5$s^5$ state is also well known for the same elements, but the intermediate state 6$s^5$ or 5$s^5$ is skipped in oxides and many other compounds. Thus, we have Ti$^{2+}$, Ti$^{3+}$; Pb$^{2+}$, Pb$^{4+}$; Bi$^{3+}$, Bi$^{5+}$; Sn$^{2+}$, Sn$^{4+}$; Sb$^{3+}$, Sb$^{5+}$; Te$^{4+}$, Te$^{5+}$; and I$^+$, I$^-$ all without the intermediate oxidation state in oxides. Compounds with compositions that seem to violate this rule are found to have a mixture of $s^0$ and $s^2$ configurations. For example, SbO$_2$ contains a 1:1 mixture of Sb$^{3+}$ and Sb$^{5+}$. Thus, the formula for this compound is normally written as Sb$_2$O$_4$. The white color of this compound indicates that promoting an $s$ electron from Sb$^{3+}(5s^2)$ to Sb$^{5+}(5s^0)$ is a high energy transition caused by the very different environments of Sb$^{3+}$ and Sb$^{5+}$ in this structure.

Skipped oxidations are common. Oxidation states for Mn up to 7+ are known. Although compounds containing Mn$^{5+}$ and Mn$^{6+}$ are known, they are generally metastable and disproportionate into Mn$^{4+}$ and Mn$^{2+}$ compounds under equilibrium conditions. These skipped oxidation states of 5+ and 6+ are easy to understand when the disproportionated products are different compounds. However, when the product of the disproportionated oxidation state is in the same compound, a difficult issue arises, that of negative U. In a simple Hubbard model for BaBi$^{4+}$O$_6$, the disproportionation of Bi$^{4+}(s^1)$ into Bi$^{3+}(s^2)$ and Bi$^{5+}(s^3)$ should not occur due the extra electron repulsion created on the $s^2$ site. A positive Hubbard U value represents the energy needed to overcome this electron repulsion occurring on the disproportionation of Bi$^{4+}$. If the disproportionation occurs spontaneously, the Hubbard U value is negative. However, the movement of O$^-$ toward Bi$^{4+}$ and away from Bi$^{3+}$ coupled with related polarization stabilize the disproportionated or –U state. Physicists and chemists often describe this situation in opposite ways. Many physicists view Bi$^{4+}$ disproportionation as caused by the very different Bi–O distances at the two Bi sites in BaBiO$_3$. Why the two sites are different is somewhat of a mystery. The view of chemists, however, is that it is the expected Bi$^{4+}$ disproportionation that has caused the Bi$^{2+}$–O and Bi$^{5+}$–O distances to become different.
1.4. Structure

The ideal AMO₃ perovskite structure (Fig. 1a) is cubic with perfect octahedral coordination for the M cation and a coordination number (CN) of 12 for the A cation. A geometric requirement of this cubic structure is that the A–O distance is equal to the M–X distance times $\sqrt{2}$. Actual sizes of the A and M cations are such that this condition is usually not well satisfied for compounds that have some version of the perovskite structure. A tolerance factor can be defined as $t = (r_A + r_O)/[\sqrt{2}(r_M + r_O)]$, where $r_A$, $r_M$, and $r_O$ are the radii of the A cation, M cation, and O anion, respectively. Most compounds with the perovskite structure have a value of $t$ less than 1.0. As $t$ decreases from 1.0, tilting of the octahedra occurs to decrease some of the A–X distances, thus decreasing the A cation CN. A systematization of the structures that can occur through this tilting of regular octahedra has been reported for both AMO₃ and A₂MM'O₆ perovskites with rock salt ordering of the M and M' cations [23]. For BaPb₁₋ₓBiₓO₃ and Ba₁₋ₓKₓBiO₃ phases the $t$ factor at room temperature is always considerably less than 1.0; thus, noncubic structures with tilted octahedra are always observed at room temperature. With increasing temperature the Ba–O distances increase, but there is no significant increase in the M–O distances. Thus, $t$ increases with increasing temperature and cubic symmetry is observed at high temperatures.

The structure of BaBiO₃ has been determined from 4.2 K to 973 K using neutron diffraction data from polycrystalline samples [8,17–19], and the structure at room temperature is shown in Fig. 1. The structure from 4.2 to 140 K is monoclinic in space group $P2₁/n$, from 140 to 430 K it remains monoclinic but now in space group $I2/m$; from 430 to 820 K it is rhombohedral in space group $R3$, and finally it is cubic in space group $Fm\overline{3}m$ above 820 K. The unit cell dimensions vs temperature are plotted in Fig. 2. Note the discontinuous nature of the monoclinic-to-rhombohedral transition. The tilt angles for the BiO₆ octahedra are plotted in Fig. 3. As temperature increases from 4.2 to 973 K, Ba–O distances lengthen considerably, but the average Bi–O distances for Bi³⁺ and Bi⁵⁺ remain 2.29 and 2.11 Å, respectively [19]. Thus, there is no indication of a weakening of the CDW as temperature increases.

The structure of BiO₂ was not known until 1995 [12]. Bi₂O₃ does not oxidize on heating in air. Preparation of Bi₂O₃ requires highly oxidizing conditions at low temperature, and on heating Bi₂O₃ in air it decomposes liberating O₂ at about 300 °C. The structure of Bi₂O₃ shows two distinct sites for Bi, which can be identified as Bi³⁺ and Bi⁵⁺. This Bi₂O₃ structure is the same as the $\beta$-Sb₂O₅ structure where the oxidation states are Sb³⁺ and Sb⁵⁺. The environment for Bi³⁺ in Bi₂O₃ is shown in Fig. 1b and compared with that found for Bi⁵⁺ in Ba₂Bi³⁺Bi⁵⁺O₆. The very low symmetry environment for Bi³⁺ in Bi³⁺Bi⁵⁺O₄ is typical of $s^2$ cations. The perovskite structure forces a higher symmetry for Bi⁵⁺.

1.5. Nonstoichiometry of BaBiO₃

Nonstoichiometry can occur with regard to the Ba:Bi ratio or the cation-to-anion ratio, but only the BaBiO₃₋ₓ situation will be discussed here. The 5+ oxidation state of Bi is thermally unstable. In the case of BaBiO₃, oxygen loss on heating in air is significant by 1170 K (Fig. 4) [24]. By 1270 K in air the composition has become BaBiO₂.₈₉, giving an average Bi oxidation state of 3.78+. Below about 1150 K the upper limit of $x$ for BaBiO₃₋ₓ phases with the CDW is about 0.03. Then there is a two phase region between regions I and II. The structure of BaBiO₂₋ₓ phases in region II remains perovskite type and is cubic with no CDW. Above about 1150 K the miscibility gap between region I and II closes and the CDW continuously weakens with increasing $x$ until it disappears. There is then another gap between region II and III. The structure of BaBiO₃₋ₓ phases in region III is not perovskite related. A structure refinement of cubic BaBiO₂.₈₉ in region II shows just one Bi–O distance of 2.213 Å [25]. This is somewhat larger than the average of the Bi³⁺–O and Bi⁵⁺–O distance (2.205 Å) found for Ba₂Bi³⁺Bi⁵⁺O₆. This expansion is expected because the average oxidation state for Bi is now less than 4+.
One group has reported that BaBiO₃ can be prepared with a much smaller difference between the Bi–O distances at the two different Bi sites [26]. Instead of a difference of about 0.15 Å found by all other groups, they find a difference of only 0.014 Å for certain samples. Their explanation was that partial disorder of Bi³⁺ and Bi⁵⁺ at high temperatures could be quenched to room temperature, although there is no evidence of any such disorder as temperature is increased unless oxygen is lost. The samples showing this difference were all first prepared as crystals at 1398 K. At this temperature the O deficiency is very high; extrapolation based on Fig. 4 would suggest a composition of about BaBiO₂.75. They believed that their samples were fully oxidized on slow cooling in air or O₂. It is very difficult to imagine any barrier that could prevent ordering of Bi³⁺ and Bi⁵⁺ for stoichiometric BaBiO₃. The structure of Ba₂Bi³⁺Bi⁵⁺O₆ is properly described as a commensurate CDW. Thus in Ba₂Bi³⁺Bi⁵⁺O₆, we are not ordering two distinct cations; we are simply ordering electrons on two distinct Bi sites. The lowest energy electron ordered state for stoichiometric BaBiO₃ is the rock salt ordering of Bi³⁺ and Bi⁵⁺, and a disordered arrangement of these cations should not be possible at room temperature for stoichiometric BaBiO₃.

When these unusual samples with the very weak CDW were annealed at 1073 K under air or O₂, the difference in the Bi–O distances between the two sites increased to values close to those found by others indicating Bi³⁺ on one site and Bi⁵⁺ on the other site. The most likely explanation is that their highly oxygen deficient crystals prepared at 1398 K did not fully oxidize on cooling to room temperature. However, grinding these crystals to powder and annealing at 1073 K led to essentially complete oxidation. Powders of BaBiO₃₋ₓ oxidize rather quickly in air. However, cooling from 1398 K in air at rates as low as 6 K/h is no assurance that crystals will fully oxidize under these circumstances. For example, complete oxidation of 2H CuScO₂ to 2H CuScO₂₃ occurs in a few hours at 700 K, but bulk oxidation of a 0.1 mm size CuScO₂ crystal did not occur after 10 days at the same conditions [27]. Only a very thin surface layer of the crystal was oxidized. The amount of oxygen deficiency causing this apparent disorder of Bi³⁺ and Bi⁵⁺ in BaBiO₃₋ₓ could be very low (x less than 0.05) and not readily detected despite the relatively good sensitivity of neutron diffraction for O content. Another issue with the crystals of this study is possible contamination from the Pt crucibles as typically happens when growing perovskite-type oxide crystals in Pt crucibles, especially when Ba is present. This problem has been known since 1959 in the growth of BaTiO₃ crystals in Pt crucibles [28]. Growing cuprate superconductors in Pt crucibles was quickly abandoned due to substitution of Pt for Cu. Even very small substitution of Pt for Bi in BaBiO₃ could weaken the CDW.

### 1.6. Properties and electronic structure

The first electrical resistivity results on a crystal of Ba₂Bi³⁺Bi⁵⁺O₆ appeared in the 1975 paper that announced superconductivity in BaPb₁₋ₓBiO₃ phases [2]. Details on resistivity as a function of temperature were published in 1979 together with structural analysis for BaBiO₃ [8]. These data were obtained from 100 to 473 K on a crystal grown hydrothermally at 973 K under high O₂ pressure in a sealed gold tube. Obtaining crystals in this way avoided any possibility of oxygen deficiency or contamination with Pt. Fig. 5 shows an abrupt break in the resistivity vs 1/T plot at the 430 K monoclinic-to-rhombohedral transition. Activation energies derived from this plot are 0.23 eV below this transition and 0.16 eV above this transition. The inset in Fig. 5 shows the
endothermic event on heating BaBiO$_3$ through the monoclinic-to-
monoclinic-to-tetragonal transition. Optical characterization of excited states 
indicate that the activation energy is consistent with a polaronic 
charge carrying state in BaBiO$_3$ [29]. It has recently been shown that 
BaBiO$_3$ is the first known oxide example of a topological insulator 
[30].

2. BaPb$_{1-x}$Bi$_x$O$_3$

As soon as it was confirmed that BaBiO$_3$ was a diamagnetic semiconductor with no metal-to-insulator transition, a metal-to-
insulator transition was sought in the BaPb$_{1-x}$Bi$_x$O$_3$ solid solution 
because BaPbO$_3$ was well known to possess metallic properties 
(Fig. 6) [31]. Attributing the lack of a band gap to O vacancies is 
unlikely because no change in the resistivity is found on annealing 
BaPbO$_3$ under high pressure O$_2$ [31]. Thus, BaPbO$_3$ appears to be a 
semimetal with slight overlap of the O 2p valence band with the Pb 6s 
conduction band. Superconductivity exists from about $x = 0.15$ to 
0.30 (Fig. 7). The initial report of superconductivity at 13 K in this 
system was based on a Meissner effect and electrical conductivity measurements using a single crystal (Fig. 8) [2]. Again the 
crystal was grown hydrothermally at high O$_2$ pressure in a gold 
tube to prevent O deficiency or contamination with Pt. The scientific 
community met this report with considerable and predictable 
skepticism. A typical response at the time of the report of super-
conductivity was “the perovskite phase (BaPb$_{1-x}$Bi$_x$O$_3$), contrary to all reports, could not be the source of 
superconductivity, based on known mechanisms of superconductivity.” [32]. Skeptical reviewers would have most likely caused a 
very considerable delay in the reporting this discovery. It was for 
this reason that the paper had been submitted in a way to circum-
vent the normal review process. A $T_c$ of 13 K was considered 
remarkable for a compound having no transition metal and for 
its very small electronic density of states at the Fermi level [33].

2.1. Structure

The perovskite-type structure prevails for BaPb$_{1-x}$Bi$_x$O$_3$ phases 
at all values of $x$. The value of $t$ decreases with increasing $x$ in 
the BaPb$_{1-x}$Bi$_x$O$_3$ system because Bi is larger than Pb. This decreasing 
$t$ is expected to cause an increase in the temperature of both 
the orthorhombic-to-tetragonal and tetragonal-to-cubic transitions as $x$ increases. Thus, cubic symmetry is obtained at 673 K 
for $x = 0.0$ but not until 820 K for $x = 1.0$. The slopes of the lines 
for these transition boundaries generally increase with increasing 
x (Fig. 7), but there appears to be a minimum at about $x = 0.2$. These 
are entropy driven phase transitions, and the disorder inherent 
in a solid solution increases the entropy and thereby lowers the 
transition temperatures apparently giving the minimum shown in 
Fig. 7.

The room temperature orthorhombic structure for BaPbO$_3$ has the 
Ibmm space group. A transition to the monoclinic $I2/m$ space group was reported to occur below room temperature, but it was 
later reported that the Ibmm space group is maintained down to 
4.2 K [34]. Above about 573 K the structure becomes tetragonal in space group $I4/mcm$ [34]. It is important to note that this 
orthorhombic-to-tetragonal transition is discontinuous; thus, some 
hysteresis is expected. The structure finally achieves cubic symmetry 
(space group $Pm3m$) above 673 K [34]. The tetragonal-cubic transition is continuous; thus, no hysteresis is expected or observed.

As $x$ increases from 0.0, the orthorhombic Ibmm symmetry is generally observed at room temperature. However, in the vicinity 
of the superconducting region, a tetragonal phase (space group $I4/mcm$) is observed, usually mixed with the Ibmm phase. At $x$ values 
exceeding the superconducting region, only the orthorhombic 
Ibmm symmetry is observed until about $x = 0.77$ where the structure 
at room temperature becomes that of monoclinic BaBiO$_3$ [35]. The ordering of Bi$^{3+}$ and Bi$^{5+}$ that occurs at $x$ values higher 
than 0.77 necessarily lowers the symmetry from orthorhombic to 
monoclinic, but the pattern of octahedral tilting does not change. 
Presumably, over the entire range of $x$ from 0.0 to 0.77, there is a 
temperature above room temperature where the tetragonal 
$I4/mcm$ exists. At still higher temperatures cubic symmetry would 
be present for all values of $x$ (Fig. 7). However, detailed structure 
investigations as a function of temperature have been reported 
only for $x = 0.0, 0.2$, and 1.0 [19,34,35].

2.2. Complex phase relationships

The phase diagram shown in Fig. 7 is likely qualitatively correct 
assuming that equilibrium is achieved and assuming that there is 
no deviation from the BaPb$_{1-x}$Bi$_x$O$_3$ formula. Based on this phase 
diagram, the tetragonal phase found in samples with $x = 0.1–0.3$ at 
room temperature is metastable but can exist all the way down 
to the temperatures where superconductivity occurs [35]. 
Normally, samples with $x = 0.1–0.3$ contain significant amounts 
of both the tetragonal and orthorhombic phases at room temperature.
The factors that stabilize the tetragonal phase at temperatures 
lower than that indicated in Fig. 7 are poorly understood at 
this time, and it is possible that the tetragonal phase is not meta-
stable at room temperature and lower temperatures. This would 
mean that the phase diagram is more complex than that shown in 
Fig. 7. Understanding this situation is crucial because it appears 
that only the tetragonal phase is superconducting. This complex 
situation is discussed in detail in Supplementary Information (SI) 
and is briefly discussed here.

In 1976 the tetragonal phase was identified as the supercon-
donducting phase in the first structural study of the BaPb$_{1-x}$Bi$_x$O$_3$ sys-
tem [7]. However, the situation is complicated by the fact that 
mixtures of tetragonal and orthorhombic phases usually occur 
for values of $x$ where superconductivity is observed. The overlap 
of diffraction peaks from the two forms is such that peaks are very 
difficult to resolve without the aid of high resolution diffraction. 
The first high resolution diffraction study of BaPb$_{1-x}$Bi$_x$O$_3$ phases 
in 1986 utilized synchrotron radiation, where the coexistence of 
the orthorhombic and tetragonal phases in the superconducting 
region was demonstrated [36]. However for a rapidly quenched sample with $x = 0.275$, the high-resolution pattern could be fit well 
assuming the presence of only the tetragonal phase (Fig. S13).
Rapidly quenched samples were also reported to produce a sharper transition to the superconducting state. In the original 1975 report on superconductivity in the BaPb$_1$-$_x$Bi$_x$O$_3$ system, it was also mentioned that partial substitution of alkali cations for Ba according to Ba$_{1-x}$A$_x$Pb$_1$-$_x$Bi$_x$O$_3$ ($A = \text{Rb, K, or Na}$) was effective in sharpening the transition [2]. This suggests that such substitutions might enhance the presence of the superconducting tetragonal phase over the nonsuperconducting orthorhombic phase, but this has apparently not been further studied.

High resolution diffraction experiments using polycrystalline samples of BaPb$_{1-x}$Bi$_x$O$_3$ and Ba$_{1-x}$K$_x$BiO$_3$ phases are hampered by peak broadening caused by lattice strain. There are two components to this strain. One is the usual strain often found in solid solutions where atoms with different sizes occupy the same crystallographic site. Solid solutions are intrinsically inhomogeneous, and strain becomes more pronounced if there is clustering. This strain occurs within individual crystallites. The second component to lattice strain results from the twinning that occurs during the cubic-to-tetragonal and tetragonal-to-orthorhombic transitions. This causes a multidomain microstructure with many incoherent grain boundaries, which cause lattice strain. This lattice strain induced peak broadening is readily distinguished from that due to crystallite size, and this broadening may be different for different peaks (anisotropic strain). In the case of BaPbO$_3$, peak broadening originally thought to be caused by a distortion to monoclinic symmetry (space group $I2/m$) was later attributed to anisotropic strain caused by twinning [34]. This twinning issue also impacts diffraction by crystals. A true single crystal grown at a temperature where the symmetry is cubic usually becomes multiply twinned on going through the cubic-to-tetragonal transition, and the twinning becomes even more complex if this crystal then undergoes a tetragonal-to-orthorhombic transition. Braden et al. discuss this twinning situation in detail for Ba$_{1-x}$K$_x$BiO$_3$ phases [37], and situation is essentially the same for BaPb$_{1-x}$Bi$_x$O$_3$ phases. Early neutron diffraction studies established lattice strain for certain BaPb$_{1-x}$Bi$_x$O$_3$ samples [7]. Pronounced strain was detected for samples with $x = 0.0$, and the strain becomes more pronounced in a sample with $x = 0.3$. This suggests that the presence of this strain may be produced by incoherent grain boundaries resulting from the cubic-to-tetragonal and the tetragonal-to-orthorhombic transitions. These transitions exist for both the cubic-to-tetragonal and tetragonal-to-orthorhombic transitions. One can expect that different microstructures will result from different thermal histories of samples.

An extensive study of BaPb$_{1-x}$Bi$_x$O$_3$ samples in 1992 by Marx et al. [35] confirmed the coexistence of the tetragonal and orthorhombic phases for $x$ values where superconductivity occurred. This study also confirmed that rapid quenching of all samples with $x = 0.2–0.3$ increases the relative amount of tetragonal phase present. The authors presented compelling evidence that the tetragonal phase is metastable at room temperature and below. For a sample with $x = 0.2$ they found that the relative amount of orthorhombic phase steadily decreases with increasing temperature from $\sim 250$ K up to $\sim 450$ K where it disappears leaving pure tetragonal phase (Fig. 9). This suggests an equilibrium orthorhombic-to-tetragonal transition at about 450 K where it disappears leaving pure tetragonal phase (Fig. 9). This suggests an equilibrium orthorhombic-to-tetragonal transition at about 450 K for this composition (Fig. 7). However, the true equilibrium temperature might be somewhat lower because some hysteresis can be expected in this first-order transition. This is then the only well established transition temperature for compositions other than $x = 0.0$ and 1.0.

Another study of the coexistence of the orthorhombic and tetragonal BaPb$_{1-x}$Bi$_x$O$_3$ phases was reported in 2011 by Climent-Pascual et al. [38]. Samples with $x = 0.0, 0.15, 0.2, 0.225, 0.25, 0.275, 0.3, 0.35$, and 0.6 were prepared by slow cooling. Superconductivity was observed only in samples with $x = 0.15–0.3$. A mixture of tetragonal and orthorhombic phases was observed in this entire superconducting region, but only the orthorhombic phase was observed in samples with higher and lower $x$ values (Figs. 10 and 11). The information presented in Fig. 11 is essentially the same as had been previously reported by Marx et al. in 1992 [35]. The percent of the samples determined to be superconducting correlated with the amount of tetragonal phase present at room temperature. This then again confirms the
conclusion of earlier studies that only the tetragonal phase is superconducting [7,35]. The relative amount of tetragonal phase is expected to decrease with decreasing temperature, consistent with the reduced volume fraction of the superconducting phase relative to the room temperature fraction of the tetragonal phase (Fig. 10). Maximum \( T_c \) occurs in the region of maximum content of the tetragonal phase. It must be emphasized that the results reported in this study are characteristic only of samples prepared as reported in this study. These samples were prepared by slow cooling, and it had been previous shown in other studies that the amount of tetragonal phase obtained for a particular value of \( x \) increases in samples rapidly cooled from the synthesis temperature [35,36].

Very recent studies of BaPb\(_1\)–Bi\(_2\)O\(_3\) crystals provides important information on the tetragonal/orthorhombic mixture in the BaPb\(_1\)–Bi\(_2\)O\(_3\) solid solution [39]. This work provides the experimental proof that superconducting BaPb\(_1\)–Bi\(_2\)O\(_3\) crystals, as normally grown, are not single crystals. Instead, electron microscopy shows an intergrowth of small tetragonal and orthorhombic domains.

A semiconductor-to-metal (S–M) transition occurs in the BaPb\(_1\)–Bi\(_2\)O\(_3\) system with decreasing \( x \) at a value of \(< 0.3\). This has widely been assumed to be related simply to Bi concentration, rather than the symmetry of the phase present. However, this S–M transition occurs with decreasing \( x \) just as the \( I4/mcm \) phase first appears at room temperature. It may be that the change to metallic properties is more related to the appearance of the tetragonal phase rather than the concentration of Bi. The semiconducting \( Ibm \) phase that exists at higher \( x \) values at room temperature may remain semiconducting for \( x \) values well below 0.3. Supporting evidence for this possibility comes from EXAFS studies [40–43]. In the Ba\(_1\)–K\(_2\)Bi\(_2\)O\(_3\) system, there is a S–M transition with increasing \( x \) and there is no complication of coexistence of two phases at the same value of \( x \). EXAFS studies in the semiconducting region (\( x = 0.2 \)) show two Bi sites with Bi–O distances indicative of a 1:1 mixture of Bi\(_{3+}\) and Bi\(_{5+}\), as in BaBiO\(_3\) [42,43]. In the metallic region (\( x = 0.4 \)) only one Bi site is observed with a Bi–O distance intermediate between that expected for Bi\(_{3+}\) and Bi\(_{5+}\). This is the behavior expected for a S–M transition occurring with increasing \( x \). In the BaPb\(_1\)–Bi\(_2\)O\(_3\) system, two Bi sites identified as Bi\(_{3+}\) and Bi\(_{5+}\) are found in the range considered semiconducting (\( x > 0.3 \)). However at \( x = 0.25 \) where the system is considered metallic, the EXAFS data cannot be well fit on the basis of one Bi site expected for a metallic phase [40,41]. This might be explained on the basis of different Bi–O distances in the coexisting \( I4/mcm \) and \( Ibm \) phases. However, if both of these phases were metallic, significantly different Bi–O distances would not be expected. It seems more likely that this is evidence that the coexisting \( Ibm \) phase remains semiconducting at \( x \) values where the \( I4/mcm \) phase is metallic and superconducting. This might then produce three Bi sites, two for the semiconducting \( Ibm \) phase and one for the metallic \( I4/mcm \) phase. A fit to three peaks could be no worse than a fit to two peaks that was used.

Two simple formulas could be assumed to describe the BaPb\(_1\)–Bi\(_2\)O\(_3\) system: metallic BaPb\(_1\)–Bi\(_{3+}\)O\(_x\) and semiconducting BaPb\(_1\)–Bi\(_{5+}\)O\(_x\). For BaPb\(_1\)–Bi\(_{3+}\)O\(_x\), \( x \) electrons are delocalized into a conduction band based on Pb 6s, O 2p, and Bi 6s states. At low \( x \) values this possibility is favored by the bonding distances for Bi and Pb. The Pb–O distance in BiPbO\(_3\) is 2.15 Å, while in BaBiO\(_3\), the Bi\(_{5+}\)–O distance is 2.29 Å and the Bi\(_{3+}\)–O distance is 2.11 Å. Therefore, Bi\(_{5+}\) is a much better fit to the BaPbO\(_3\) lattice than is Bi\(_{3+}\). Thus at low values of \( x \), Bi might be considered simply as Bi\(_{5+}\) and a donor of electrons to the Pb 6s conduction band. As the lattice expands with increasing \( x \), a transition from metallic BaPb\(_1\)–Bi\(_{3+}\)O\(_x\) to semiconducting BaPb\(_1\)–Bi\(_{5+}\)O\(_x\) may occur at an \( x \) value significantly less than 0.25 for the \( Ibm \) phase. Charge ordering has also been associated with the \( Ibm \) space group in the case of some A(Mn\(_{3+}\),Mn\(_{5+}\))O\(_3\) perovskites [44]. Furthermore, recent group theoretical considerations led to the conclusion that charge ordering should occur in space group \( Ibm \) but not in \( I4/mcm \) [45]. Critical questions remain unanswered. What is the range of \( x \) with metallic properties for the BaPb\(_1\)–Bi\(_2\)O\(_3\) phase, considering that BaPbO\(_3\) itself shows metallic properties? Is there a S–M, \( Ibm \)-to-\( I4/mcm \) transition with increasing temperature for some range of \( x \)? Electrical measurements on a BaPb\(_1\)–Bi\(_2\)O\(_3\) crystal as a function temperature for an \( x = 0.35 \) sample might give an answer. However, the change in resistivity expected through such a transition is small. Measurements on sintered polycrystalline samples of metallic BaPb\(_1\)–Bi\(_2\)O\(_3\) (\( x = 0.0–0.1 \)) indicate a room temperature conductivity less than a factor of ten higher than a semiconducting sample with \( x = 0.3 \) [35,46]. The conductivity change would be even smaller at the higher temperature where the transition would occur. Furthermore because this is a first-order transition, different parts of the sample would transform at somewhat different temperatures, leading to a diffuse transition. EXAFS as function of temperature and \( x \) might help resolve this issue.

A critical question in the BaPb\(_1\)–Bi\(_2\)O\(_3\) system is understanding why the \( I4/mcm \) and \( Ibm \) phases coexist over such a wide range of \( x \) and temperature, especially since there apparently would be no superconductivity in this system if the \( I4/mcm \) phase did not exist at much lower temperatures than expected based on Fig. 7. Other perovskite phases where there is a transition from \( I4/mcm \) and \( Ibm \) are discussed comprehensively in SI. This issue is briefly described here. A transition from \( Ibm \) to \( I4/mcm \) is observed with increasing temperature at \( \sim 140 \) for SrMoO\(_3\), \( \sim 280 \) K for BaTbO\(_3\), \( \sim 560 \) K for BaPbO\(_3\), \( \sim 625 \) for SrTcO\(_3\), \( \sim 840 \) for SrRuO\(_3\), \( \sim 1060 \) K for SrSnO\(_3\), and \( \sim 1110 \) K for SrZrO\(_3\) (Figs. S1–S6). In all cases, a coexistence range of the \( I4/mcm \) and \( Ibm \) phases is either not detected or detected only over a few degrees. A small coexistence range is expected when a phase transition is discontinuous (first-order) as it must be for any \( Ibm \)-to-\( I4/mcm \) transition. However, this coexistence range may be too small to be readily detected. The only known cases of extended coexistence of the \( I4/mcm \) and \( Ibm \) phases occur where there are two different cations on one of the two cation sites. This is a compelling indication that large coexistence ranges are due, at least in part, to the inhomogeneity intrinsic to this situation, such as any solid solution. The behavior most resembling that of the BaPb\(_1\)–Bi\(_2\)O\(_3\) system is found in the Sr\(_1\)–Ba\(_2\)HfO\(_3\) system [47,48]. For the Sr\(_1\)–Ba\(_2\)HfO\(_3\) system there is room temperature coexistence of the \( I4/mcm \) and \( Ibm \) phases from about \( x = 0.50 \) to 0.65. This coexistence exists over at least 200 K with the relative amount of the \( I4/mcm \) phase decreasing with decreasing temperature. All of these results are readily explained on the basis of an inhomogeneous distribution of Sr and Ba in a system that appears to be close to equilibrium. Details on this and other solid solutions are presented in SI.

The explanation for \( I4/mcm \)-\( Ibm \) coexistence in the Sr\(_1\)–Ba\(_2\)HfO\(_3\) system does apply to the BaPb\(_1\)–Bi\(_2\)O\(_3\) system. The lattice constant vs \( x \) plot given by Climent-Pascual et al. (Fig. 11) and earlier by Marz et al. [35] clearly demonstrates the lack of equilibrium in the BaPb\(_1\)–Bi\(_2\)O\(_3\) system. The lattice constants of both the tetragonal and orthorhombic phases increase with increasing \( x \) throughout their coexistence range. This and the behavior of the unit volumes of the two phases indicate that \( x \) values are essentially the same in the two phases. These two phases cannot coexist at equilibrium, if they truly have the same composition. We might explain the coexistence of the \( Ibm \) and
H/4/mcm phases simply based on the fact that the transition between these two phase must be discontinuous (first-order). Some region of non-equilibrium coexistence is expected. A BaPb$_{0.9}$Bi$_{0.2}$O$_3$ sample was found to be single phase H/4/mcm at 450 K and became a mixture of H/4/mcm and Ibmm below this temperature, but this transition to Ibmm ceased at ~250 K leaving ~55% of the sample in H/4/mcm symmetry (Fig. 9) [35]. Such a large range of coexistence is unprecedented when the two phases have the same composition, as they apparently do in this case. The lattice strain caused by twinning and intergrowth of phases with different cell edges might be factor in inhibiting this transition. However, the fact that phase coexistence does not occur over a large temperature range for any simple AMO$_3$ perovskite with the Ibmm-to-H/4/mcm transition argues that there must be another factor involved. This could be the way in which Bi is distributed over the octahedral sites. However, it does not seem to be a situation of Bi rich and Bi poor regions, which is the type of situation in the Sr$_1$-$_x$Ba$_x$HfO$_3$ system mentioned above, because the indications are that the coexisting phases in the BaPb$_1$-$_x$Bi$_x$O$_3$ system have the same value of x. Ordering of two cations on octahedral sites is known for the perovskites Ba$_4$Li$_5$O$_{12}$ and Ba$_4$Na$_5$O$_{12}$ [47], which is then just the Bi-to-Pb ratio where superconductivity optimizes for BaPb$_1$-$_x$Bi$_x$O$_3$ phases. Although long range order of Bi and Pb may be unlikely for BaPb$_1$-$_x$Bi$_x$O$_3$ phases, there is some suggestion that it may occur (see SI). The relative stability of the Ibmm and H/4/mcm phases could be related to regions of different Pb/Bi short range order, which could explain the large range of two phase coexistence. The tetragonal phase could still be regarded as metastable at room temperature and below. Another factor that is likely related to the coexistence issue is that the MO$_6$ octahedra (M = Pb,Bi) apparently become distorted just in the region of x where this coexistence is found (see SI).

An easy way to explain the large phase coexistence region is to assume a deviation from the ideal BaPb$_1$-$_x$Bi$_x$O$_3$ formula. And the only good candidate for this would seem to be oxygen deficiency. BaPb$_1$-$_x$Bi$_{1.3}$-$_x$O$_3$. There are indications that the oxygen content should be considered a variable for the BaPb$_1$-$_x$Bi$_{1.3}$-$_x$O$_3$ samples routinely prepared. Titration studies indicate deviations from 4.0 for the average oxidation state of Pb and Bi that vary with x and annealing conditions [48]. Furthermore, this study found a significant difference in the T$_c$ for samples annealed at different temperature or different O$_2$ partial pressure. Oxides of Bi are well known for high O$^2-$ mobility; thus on cooling, any O vacancies could concentrate in certain regions, leaving other regions less concentrated. Coexistence of the H/4/mcm and R3c phases is observed from 4 to 300 K for the perovskite La$_{0.75}$Sr$_{0.30}$MnO$_{3-\delta}$, and the oxygen vacancies are concentrated in the H/4/mcm phase [49]. Any concentration of O vacancies in the H/4/mcm phase of BaPb$_1$-$_x$Bi$_{1.3}$-$_x$O$_3$ would be much less than the La$_{0.75}$Sr$_{0.30}$MnO$_{3-\delta}$ situation, but they still might be adequate to stabilize H/4/mcm relative to Ibmm. This would offer then offer an explanation for the extensive phase coexistence, and the H/4/mcm phase would not be considered metastable because it would have a different composition than that of the Ibmm phase. Because real samples would have a range of y values rather two discrete values, the gradual increase of the H/4/mcm phase relative to the Ibmm phase for BaPb$_{0.8}$Bi$_{0.2}$O$_3$ from ~250 K to ~450 K is now easy to understand (Fig. 9). But this is just speculation without further experimental data.

Phase relationships for superconducting Ba$_{1-x}$K$_x$BiO$_3$ phases were not well understood until a study that included X-ray diffraction on crystals combined with high resolution X-ray and neutron diffraction on powders [37]. Phase relationships for BaPb$_{0.8}$Bi$_{0.2}$O$_3$ phases are much more complex. A complete understanding will require an even more intense effort. Other characterization, such as electron microscopy and EXAFS, are required. These are needed as a function of x on samples prepared under varying oxygen pressure and cooling rates. More structural studies are required as a function of temperature, starting with the high temperature cubic phase and continuing down in temperature to the region where superconductivity occurs. There is no reason at this time to conclude that it is impossible to obtain pure tetragonal BaPb$_{1-x}$Bi$_x$O$_3$ phases at room temperature. This appears to have occurred for a BaPb$_{0.9}$Bi$_{0.1}$O$_3$ crystal and a quenched sample of BaPb$_{0.75}$Bi$_{0.25}$O$_3$ (Fig. S13) [36,50], but the ultimate goal is to produce tetragonal BaPb$_{1-x}$Bi$_x$O$_3$ phases that remain single phase down to temperatures at which superconductivity occurs.

2.3. Properties

A S–M transition occurs with decreasing x for BaPb$_{1-x}$Bi$_x$O$_3$ compositions, and the value of x for this transition is frequently given as ~0.3. However, electrical resistivity for sintered compacts decreases with increasing temperature down to x = 0.25, and resistivity vs temperature is essentially flat when x = 0.2, a result reproduced by different groups [35,46]. Based on these results, the S–M transition appears to occur at an x value of ~0.2. The highest T$_c$ for superconductivity at x = ~0.25 would then lie well within the semiconducting region. It appears, however, that the superconducting tetragonal phase is always metallic, and the semiconducting behavior observed in superconducting samples is due to an admixture with the semiconducting orthorhombic phase. The first report of electrical resistivity for a superconducting BaPb$_{1-x}$Bi$_x$O$_3$ composition was on a crystal that showed resistivity above T$_c$ increasing with increasing temperature as expected for a metal (Fig. 8) [21].

The pervasive lack of phase purity for superconducting BaPb$_{1-x}$Bi$_x$O$_3$ samples means that much of the characterization of these samples is of dubious value. This problem is not circumvented with crystals because the crystals are usually not single crystals; they also contain a mixture of the tetragonal and orthorhombic phases. This phase purity issue is apparently absent for Ba$_{1-x}$K$_x$BiO$_3$ superconducting compositions. Thus, we delay further discussion of properties to the section where the properties of Ba$_{1-x}$K$_x$BiO$_3$ phases are considered.

3. Ba$_{1-x}$K$_x$BiO$_3$

Although substitutions for Ba by K, Cs, Rh, Na, and Sr had been reported in 1976 for BaPb$_{1-x}$Bi$_x$O$_3$ phases [2,51,52], attempts at that time by several groups failed to prepare Ba$_{1-x}$K$_x$BiO$_3$ phases.
Traces of a superconducting Ba$_{1-x}$K$_x$BiO$_3$ phase with a $T_c$ of about 20 K was reported in 1988 [3]. This 12 year delay was caused by the fact that the conventional synthesis approach of heating reactant oxides, carbonates, or nitrates in air or O$_2$ does not produce a Ba$_{1-x}$K$_x$BiO$_3$ perovskite phase. The first successful synthesis of a bulk sample of the Ba$_1$K$_x$BiO$_3$ superconductor utilized BaO, KO$_2$, and Bi$_2$O$_3$ in Ag tubes sealed in evacuated silica tubes [4]. Both BaO and KO$_2$ are difficult reactants to work with. This oxygen deficient product was then annealed under flowing O$_2$ to achieve Ba$_{0.6}$K$_{0.4}$BiO$_3$, which was found to be superconducting at 30 K. Ba$_{0.6}$K$_{0.4}$BiO$_3$ was prepared by a similar method and found to become superconducting at 29 K. Other methods to synthesize these materials have been subsequently described. A preferred synthesis route now is the electrodeposition method long known for producing crystals of cubic KBiO$_3$ [11,53].

The size of K is slightly larger than that of Ba$^{2+}$, and the size of Bi decreases with increasing x as its average oxidation state increases. Thus, t increases with increasing x, ultimately resulting in a cubic structure at room temperature. A proposed phase diagram for the Ba$_{1-x}$K$_x$BiO$_3$ system is shown in Fig. 12. This has been constructed mainly from results of Marx et al. and Braden et al. [35,37]. KBiO$_3$ is known, but not with the perovskite structure [11]. The highest value of x for which the perovskite structure has been observed is about 0.5. Superconductivity is observed with x values from about 0.3 to 0.45. A maximum $T_c$ of 34 K occurs at an x value of about 0.35. The room temperature structure of Ba$_{1-x}$K$_x$BiO$_3$ superconducting phases is cubic. Thus, it was initially assumed that superconductivity only occurs in cubic Ba$_{1-x}$K$_x$BiO$_3$ phases. However, it was later established that the symmetry of all Ba$_{1-x}$K$_x$BiO$_3$ phases at the temperature where they are superconducting is actually tetragonal (I4/mcm) [37], which is then the same space group as for the BaPb$_{1-x}$Bi$_x$O$_3$ superconducting phases. The same metastability issue potentially arises for both the BaPb$_{1-x}$Bi$_x$O$_3$ and Ba$_{1-x}$K$_x$BiO$_3$ systems. The cubic-to-tetragonal transition is continuous, but the tetragonal-to-orthorhombic transition is discontinuous. If the equilibrium temperature of this tetragonal-to-orthorhombic is too low, it might simply not occur. In this case, superconductivity would only be occurring in a tetragonal Ba$_{1-x}$K$_x$BiO$_3$ metastable phase as is the case for BaPb$_{1-x}$Bi$_x$O$_3$.

### 3.1. Properties

Table 3 summarizes some relevant properties for Ba$_{1-x}$K$_x$BiO$_3$ superconductors. Initially, the resistivity of Ba$_{1-x}$K$_x$BiO$_3$ phases above $T_c$ was reported to decrease with increasing temperature. However, these measurements were on polycrystalline materials. When crystals became available, measurements of resistivity above $T_c$ was shown to increase with increasing temperature, as expected for a metal [59]. Thus, in neither the BaPb$_{1-x}$Bi$_x$O$_3$ nor Ba$_{1-x}$K$_x$BiO$_3$ systems do we actually have an anomalous temperature dependence of electrical resistivity in the normal state, as was frequently reported in both systems. Hall effect measurements indicate an electron carrier concentration consistent a Bi 6s band that is about 35% filled [59].

![Image](image_url)

**Fig. 13.** Structure of KBa$_3$Bi$_4$O$_{12}$ where the K site actually contains some Na as well as K and some vacancies. Green K site spheres, black Ba spheres, red O spheres, and blue BiO$_3$ octahedra. Despite the cubic symmetry, the Bi octahedra are now slightly tilted [62]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

**4. Related compositions**

Since the discovery of superconductivity in BaPb$_{1-x}$Bi$_x$O$_3$ phases, there have been many attempts to find superconductivity in related systems. Most of this work has not been published because it did not produce superconductors or anything else worthy of a publication. The most notable exception produced superconductivity in Ba$_{1-x}$A$_x$BiO$_3$ phases where A is K or Rb [3,4]. It was subsequently the found that Ba could be replaced with Sr, and $T_c$ as high as 12 K was obtained [61]. Many superconducting compositions with the formula Ba$_{1-x}$A$_x$Pb$_{1-y}$Bi$_y$O$_3$ have also been reported [35].

The composition (K$_{0.43}$Na$_{0.25}$)Ba$_2$Bi$_4$O$_{12}$ with a perovskite-type structure was recently reported with $T_c$ of 27 K [62]. This is the first report of ordering of cations at the A site for these materials (Fig. 13). Note that the K/Na site is 30% vacant. This result suggests

![Image](image_url)

**Fig. 14.** Partial density of states for α-Bi$_2$O$_3$. Darkest line for Bi 6s states, lightest line for Bi 6p states and intermediate shade for O 2p states [72].
the possibility that a significant concentration of A site vacancies may be present is some superconducting phases reported as Ba$_{1-x}$A$_x$BiO$_3$. The peaks produced in X-ray diffraction patterns by this larger unit cell are very weak and could be missed. Another superconducting composition reported with the perovskite type structure is (Ba$_{0.75}$K$_{0.14}$H$_{0.11}$)BiO$_3$ with a $T_c$ of 8 K [63].

Compositions of the type BaPb$_{1-x}$Sb$_x$O$_3$ produce superconductors with a $T_c$ as high as 3.5 K [64]. Analogous substitutions using Nb or Ta for Sb have not produced superconductors. Likewise, attempts to prepare BaSn$_{1-x}$Sb$_x$O$_3$ superconductors have not produced positive results.

There are many examples of mixed oxidation states of elements in the $s^0$ and $s^2$ configurations. Most are insulators, like white Sb$^3$Sb$^{5+}$O$_4$. Recent work on mixed Te$^{4+}$/Te$^{6+}$ oxides has produced black phases with appreciable electronic conductivity [65–67]. For example, compositions of the type CsTe$_2$O$_6$, with a pyrochlore-type structure were studied from $x = 0.0$ to 1.5. This covers a range of average Te oxidation states from +4.35 to +5.5. The CsTe$_2$O$_6$ composition shows well ordered Te$^{4+}$ and Te$^{6+}$ with a formula Cs$_2$Te$^{4+}$Te$^{6+}$O$_{12}$, where Te$^{4+}$ and Te$^{6+}$ are on distinct

Fig. 15. (a) Partial DOS for Ba$_3$Bi$^{3+}$Bi$^{5+}$O$_6$ decomposed over Bi$^{3+}$, Bi$^{5+}$ and O. (b) DOS difference between Bi$^{3+}$ and Bi$^{5+}$ decomposed into 1 quantum numbers [74].

Fig. 16. (a–c) Evolution of the density of states (DOS) on Bi$^{3+}$ (orange) and Bi$^{5+}$ (blue) atoms with K hole doping x for the nonpolaronic solution. The light-gray shadows indicate the total DOS. (d) Evolution of the DOS of hole-doped BaBiO$_3$ simulated by removing a fraction of an electron (x) leading to a reduction of the gap between the Bi$^{3+}$ (orange) and Bi$^{5+}$ (blue) subbands, and the simultaneous reduction of the Bi-O bond length difference b between Bi$^{3+}$ and Bi$^{5+}$ sites. The symbols represent the estimated values of the breathing distortion b computed from the Rice and Wang gap equation [75]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 17. Evolution of the DOS and corresponding band structure for Ba$_{1-x}$K$_x$BiO$_3$ in a polaronic solution. Yellow indicates states associated with Bi$^{3+}$ and blue indicates states associated with Bi$^{5+}$. The red curves indicate the bipolaronic states created by doping [75]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
octahedral sites. The situation is very much like Ba$_2$Bi$^{5+}$Bi$^{5+}$O$_6$ in that the $s^2$ cation is in the center of a regular octahedron instead of the distorted environment usually expected for an $s^2$ cation. This compound is black and semiconducting with an activation energy of 0.64 eV. Increasing $x$ disrupts the ordering of Te$^{4+}$ and Te$^{6+}$, but semiconducting behavior remains. Higher conductivity ($\sim 0.3 \Omega^{-1} \text{cm}^{-1}$ on pellets) is obtained on substitutions into the Te site, but metallic properties are never observed.

Compounds of the type A$_2$Ti$^4$Ti$^4$X$^6$ ($A = \text{Rb or Cs}; X = \text{F, Cl, or Br}$) have a perovskite-type structure and can be considered analogues of BaBiO$_3$. However, there are no reports of metallic or superconducting properties on appropriate doping of any of these phases [68–70]. However, it has been suggested that superconductivity in Ti doped PbTe ($T_c \sim 1 \text{ K}$) is related to the presence of mixed valent Ti [71]. The skipped $s^1$ oxidation state does exist in some highly covalent compounds with the NaCl structure. Superconductivity occurs in In$^{3+}$Te ($T_c \sim 4 \text{ K}$), Sn$^{3+}$As ($T_c = 3.6 \text{ K}$), Sn$^{5+}$Sb ($T_c = 2.3 \text{ K}$), Ge$^{5+}$P ($T_c = 4 \text{ K}$), and Ge$^{5+}$As ($T_c = 3.5 \text{ K}$). In this case, the disproportionation of the $s^1$ state is frustrated, requiring disruption of cubic symmetry.

5. Theory

In oxides of Bi$^{3+}$, the Bi $6s$ states normally are predominately below the O $2p$ band as shown in Fig. 14 for $\alpha$-Bi$_2$O$_3$ [72,73]. However, a significant concentration of Bi $6s$ states exists at the top of the valence band together with the O $2p$ states. In Ba$_2$Bi$^{5+}$Bi$^{5+}$O$_6$, the Bi $6s$ states remain predominantly well below the O $2p$ states, but the $6s$ states at the top of the valence band, which are associated with Bi$^{3+}$, have moved up in energy relative to the O $2p$ band Fig. 15 [74]. Two factors would seem important for this change. One is the usual lone pair distortion expected for $s^2$ cations does not occur for Bi$^{3+}$ in Ba$_2$Bi$^{5+}$Bi$^{5+}$O$_6$. This increases the antibonding nature of the Bi $6s$–O 2p interaction and raises the energy of these Bi $6s$ states. A second factor relates to the indirect impact of the highly ionic Ba$^{2+}$ cations. This strong electrostatic field stabilizes O $2p$ states causing them to move down in energy. The empty $6s$ states due to Bi$^{5+}$ have moved even further up in energy because the Bi$^{5+}$–O distance is considerably shorter than the Bi$^{3+}$–O distance. The impact of hole doping of Ba$_2$Bi$^{5+}$Bi$^{5+}$O$_6$ is shown in Fig. 16 [75].

The discovery of superconductivity in the BaPb$_{1-x}$Bi$_x$O$_3$ system immediately led to the idea that the bipolaron implicit in the CDW description for BaBiO$_3$ was related to the occurrence superconductivity in the BaPb$_{1-x}$Bi$_x$O$_3$ system [76,77]. Other terms used to describe this bipolaron situation are “disproportionation of unstable Bi$^{4+}$”, “missing or skipped oxidation states” and “negative Hubbard U” [78]. Although there has been considerable theoretical support for a relationship of bipolarons and negative U with superconductivity [76–80], a complete theoretical understanding has only slowly developed over the last 25 years. A recent ab initio study indicates that in hole doped BaBiO$_3$, Bi$^{3+}$ sites can trap two holes from the valence band to form Bi$^{5+}$ cations [75]. This provides an explanation of why hole-doped BaBiO$_3$ remains semiconducting upon moderate hole doping (Fig. 17). A recent modified approach to calculating electron–phonon coupling indicates that the high $T_c$ obtained for bismuthates is consistent with a bipolaron model [81].

Recently, group theoretical methods were used to evaluate the interplay between octahedral rotations and electronic charge ordering in the Ba$_3$K$_2$BiO$_6$ system. The conclusion was that phases with the $\text{Ih}$ space should be insulating, but those with the $\text{Ih}$ space group can be metallic and superconducting [45].

Experimental studies indicate that superconductivity in BaPb$_{1-x}$Bi$_x$O$_3$ and Ba$_2$-K$_x$BiO$_3$ phases has never been observed in the simple cubic structure, frequently assumed in theoretical studies. Instead, the octahedra are always tilted leading to nonlinear Bi–O–Bi linkages. Recent theory seems to be beginning to give us an understanding this impact of bending the O–Bi–O linkage [82]. In this regard, it is relevant to consider a large class of oxide superconductors known as the tungsten bronzes. These phases can be represented as A$_2$MO$_3$ where M can be W, Re, or Mo; and A can be Na, K, Rb, NH$_4$, etc. (Table 1). Compounds with the simple cubic variation of this perovskite structure with linear M–O–M linkages are generally metallic, but they do not show superconductivity. Superconductivity is only observed in tetragonal and hexagonal tungsten bronzes where the M–O–M linkages are distinctly nonlinear. There has been no explanation in theory for this observation.

6. Comparison to cuprates

There are several commonalities between the superconducting cuprates and bismuthates. The starting point in both cases is based on a half-filled band, a 6s band with Bi oxides and a 3$d_{z^2}$–$y^2$ band for Cu oxides. In both cases this band splits giving an insulator, but for different reasons. The insulating state is based on a CDW in the case of BaBiO$_3$ and an antiferromagnetic ordering of Cu unpaired electrons in cuprates. However, a CDW has been found in underdoped cuprates [84]. Although the valence skipping behavior characteristic of Bi is not known for Cu, it is common for the other two elements in this column of the periodic table. AgO is not Ag$^{2+}$O, but is instead Ag$^{3+}$Ag$^{3+}$O$_2$. In the case of Au, essentially all compounds that might appear to contain Au$^{3+}$ actually contain a mixture of Au$^{+}$ and Au$^{3+}$.

Another apparent commonality between cuprate and bismuthate superconductors may be a lack of thermodynamic stability [83]. Insulating YBa$_2$Cu$_3$O$_y$ is thermodynamically stable, but upon interaction with oxygen the superconducting YBa$_2$Cu$_3$O$_y$ product is not thermodynamically stable. There is no condition of temperature and pressure for which YBa$_2$Cu$_3$O$_y$ is thermodynamically stable. This lack of thermodynamic stability has no repercussions for YBa$_2$Cu$_3$O$_y$ in terms of its practical stability once formed. The cuprates containing Bi, Tl, or Hg that superconduct at higher temperatures have a different route to metastability. They are presumably thermodynamically stable at the temperatures where they are synthesized, but they are defect and stabilized by entropy. They never actually have ideal compositions and structures generally attributed to them. As temperature is decreased from the synthesis condition, these phases become thermodynamically unstable long before they become superconducting [84]. This lack of thermodynamic stability is not limited to oxides. The superconducting AMO$_3$S$_2$ phases where A = Sn or Pb are also metastable [85,86]. The superconducting phase in the BaPb$_{1-x}$Bi$_x$O$_3$ system may also be metastable at temperatures where superconductivity occurs, but metastability of the tetragonal superconducting phase in the Ba$_3$-K$_2$O$_3$ system is less likely.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.physc.2015.02.012.


