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Laboratory Partnership Abstract
The project investigated superconductivity in non-cuprate materials with critical temperatures, \( T_c \), in excess of 20 K in order to understand the thermodynamics of several of these materials. The project is a cooperative effort between investigators at Southern University (SU), Louisiana State University (LSU), and Los Alamos National Laboratory (LANL). It involved synthesis of high quality samples, and subsequent detailed magnetic, thermal and electrical measurements on them. The project provided a PhD Thesis research experience and training for a graduate student, Ms. Robin Macaluso. High quality, single crystal samples were synthesized by Ms. Macaluso under the direction of one of the CO-PIs, John Sarrao, during the summer while she was a visitor at LANL being supported by this grant. On these samples magnetic measurements were performed at SU, thermal and electrical measurements were made in the LSU Physics and Astronomy Department. The crystallographic properties were determined in the LSU Chemistry Department by Ms. Macaluso under the direction of her dissertation advisor, Dr. Julia Chan. Additional high field magnetic measurements on other samples were performed at the National High Magnetic Field Laboratory (NHMFL) both in Tallahassee and at LANL. These measurements involved another graduate student, Umit Alver, who used some of the measurements as part of his PhD dissertation in Physics at LSU.
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Summary of Accomplishments
The following is a partial summary of the major accomplishments from the project.

(1) Crystal growth.
High quality single crystals of $\text{Ba}_1\text{K}_2\text{BiO}_3$ and $\text{Ba}_{1-x}\text{Rb}_x\text{BiO}_3$ ($x = 0.4$), and $\text{Ba}_{0.25}\text{Rb}_{0.25}\text{BiO}_3$ were grown electrochemically using a three-electrode crystallization method. Fig. 1 shows a schematic of the experimental setup developed during the grant period.

![Potentiostat diagram](image)

Fig. 1

Typical crystals produced possess cubic morphology, reflecting the cubic crystal structure ($\text{Pm3m}$ space group). The crystals are large and individual cubes are visible with the naked eye.

![Cubic crystal](image)

Fig. 2 The $\text{Pm3m}$ space group

SQUID magnetization measurements of the $\text{Ba}_{0.25}\text{Rb}_{0.25}\text{BiO}_3$ showed a superconducting transition temperature close to 26 K.

(2) X-ray structure determinations.
Structure of $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ determined from x-rays at LSU.
A sample of $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ underwent resonant ultrasound measurements as a function of temperature at Los Alamos National Laboratory. The initial cooling measurements showed a surprising result that there is a first order hysteretic phase transition in this cubic perovskite high $T_c$ material near 200 K that gives rise to a large change in both the
sound attenuation and frequency dispersion. Detailed x-ray structure determinations as a function of temperature were carried out through this new transition.

(3) Magnetic and thermal measurements.
There is an ongoing question of the thermodynamic order of the superconducting transition in Bao.6Ko.4BiO3 (BKBO). We investigated alloys of BKBO and Bao.75Rb0.25BiO3 in an attempt to lower Tc to a point where the phonon contribution to the specific heat is much smaller without changing the crystallographic structure of the material. Results from one of the samples of Bao.73Rb0.25BiO3 show the superconducting transition in the magnetization, but not in the specific heat. (Figures 3 and 4) BKBO show similar results.

Figure 3. Magnetization vs. Temperature of single crystal Bao.75Rb0.25BiO3 showing the superconducting transition.

Figure 4. Specific heat vs. Temperature of single crystal Bao.75Rb0.25BiO3 showing practically no structure near the superconducting transition at 20 K.

(4) Temperature dependence of the crystallographic parameters.
Structurally Bao.6Ko.4BiO3 (BKBO) is interesting because no CuO planes exist to mediate superconductivity. BKBO has the highest Tc (31 K at x = 0.4) in this family of compounds. A related superconducting compound (Tc = 13 K), Bao.73Pb0.27BiO3, also has a cubic perovskite structure. The crystal structure of BaPbBiO3 is known to undergo transformations from orthorhombic → tetragonal → orthorhombic → monoclinic as a function of x and superconductivity is confined to the tetragonal phase.

Published results of neutron diffraction studies on single-crystal BKBO indicate an I4/mcm space group at 50 K. Examination by powder diffraction technique on crushed single crystals using synchrotron radiation show the same space group. At T = 300 K powder neutron diffraction data shows the compound is in Ibmnn space group. The crystal structures of Ibmnn and Pm3m space groups are shown in Figures 5a and 5b.
We carried out single-crystal X-ray diffraction on a BKBO crystal, and our thermal parameters are consistent with published results. However, our refined model fits best with the Pm3m space group at temperatures between 110 K and 300 K. Lattice parameters and $R_w$ values are given in Table 1.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Lattice Parameter (Å)</th>
<th>$R$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>110</td>
<td>4.2729</td>
<td>5.7</td>
</tr>
<tr>
<td>150</td>
<td>4.2800</td>
<td></td>
</tr>
<tr>
<td>175</td>
<td>4.2775</td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>4.2800</td>
<td></td>
</tr>
<tr>
<td>225</td>
<td>4.2797</td>
<td></td>
</tr>
<tr>
<td>250</td>
<td>4.2802</td>
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</tr>
<tr>
<td>299</td>
<td>4.2826</td>
<td>4.6</td>
</tr>
</tbody>
</table>

The oxygen thermal parameters ($U_{33}$) have been measured at various temperatures in an attempt to identify any octahedral tilts and/or distortions. The thermal parameters measured are compared to those measured by Braden et al. in Figure 6.
(5) Other materials.
We synthesized BeB$_{2.75}$ and measured the electron transport properties. Our sample is superconducting below $T_c = 0.72$ K with a critical field of $H_{c2} = 0.175$ T. See Fig. 7.

Figure 6. Braden’s data in green circles. In that neutron analysis the thermal parameters of oxygen were constrained to be identical.

Figure 7. Specific heat divided by Temperature vs. Temperature squared showing that the superconducting transition near 0.7 K is clearly observed.
In addition to the work on which we have reported at the end of each reporting period, and described above, considerable effort was made in crystal growth (by Ms. Macaluso at LANL) and characterization of a new set of highly correlated superconducting and magnet materials: \((\text{Ce},\text{La})\text{MIn}_5\) where \(M = \text{Co}, \text{Ir}, \text{or Rh}\), known as the 115s. The funds provided by the grant have led to many successful cooperative projects on the 115s and other superconductors between one of the principal investigators, Roy G. Goodrich and the group led by another of the principal investigator at LANL, John L. Sarrao. Other collaborations between Goodrich and groups at LSU also were productive. The papers resulting from work during the award period are listed below in reverse chronological order.

**Publications and collaborations.**


**Number of Undergraduates Supported by DOE**

None (0)

**Number of Graduates Students Supported by DOE**

One (1)

**Number of Postdoctoral Fellows Supported by DOE**

None (0)