X-RAY DIFFRACTION STUDY OF HIGH Tc SUPERCONDUCTORS AND RELATED PHASES AT HIGH PRESSURES

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ABSTRACT

The compressive behaviors of several high Tc and related phases in the Ba-R-Cu-O system (where R is yttrium and lanthanides) and in the Ba-Hg-Cu-O system were investigated by using a diamond anvil high pressure cell and energy dispersive x-ray powder diffraction. The pressure dependence of the cell volume of the orthorhombic Ba2YCu3O6+x and BaLu2CuO5, and the tetragonal BaNd2CuO5 phases were found to be of first order. While BaNd2CuO5 exhibits nearly isotropic compressive c/a behavior, BaLu2CuO5 shows somewhat anisotropic c/a and c/b behavior. The bulk modulus of BaLu2CuO5 was determined to be 251 ± 13 GPa (standard uncertainty), which is significantly greater than that of BaNd2CuO5 161 ± 8 GPa and of Ba2YCu3O6+x (reported values ranging from 96 to 196 GPa). The tetragonal HgBa2CuO4+x behaves similarly to other layered high Tc materials under pressure in that the c-axis exhibits higher linear compression than the a-axis. The bulk modulus of this Hg-compound (94.7 ± 4.2 GPa) agrees reasonably well with reported theoretical values. No evidence of a pressure-induced phase transformation was found in any of the compounds studied in the pressure range measured.

INTRODUCTION

Mechanical reliability is an important issue that governs the successful applications of high Tc materials. To estimate toughness of a material quantitatively, it is necessary to know the value of Young's modulus for the solid [1], which can in turn be obtained from the bulk modulus, or its inverse, the compressibility. This paper discusses the relationships between compressibility and...
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and related phases in the BaO-R$_2$O$_3$-CuO (R=lanthanides and Y) and BaO-HgO-CuO systems using data obtained from high pressure x-ray powder diffraction experiments.

It is known that poor mechanical properties of the high T$_c$ material, Ba$_2$YCu$_3$O$_{6+x}$, have hindered its development into versatile practical use. Any processing route to improve its mechanical properties will be important for the superconductor industry. It was also found that BaY$_2$CuO$_5$ (also called the 121 phase or the green phase) has a significant impact on the processing of Ba$_2$YCu$_3$O$_{6+x}$ [2-5]. During solid state processing of Ba$_2$YCu$_3$O$_{6+x}$, BaY$_2$CuO$_5$ often exists as an impurity phase [2]. Also, in order to obtain superconducting materials with high J$_c$ values, BaY$_2$CuO$_5$ was often added to enhance texturing and flux pinning [3,4]. It is also been reported that the strength of Ba$_2$YCu$_3$O$_{6+x}$ appears to be increased with the presence of this 121 phase [5]. The possible role of the 121 phase in strengthening the Ba$_2$YCu$_3$O$_{6+x}$ superconductor is, however, not clear. The 121 phase, BaR$_2$CuO$_5$, has two different structure types [6]. With R = Sm, Gd, Dy, Ho, Er, Tm, Yb and Lu, the color of this orthorhombic compound is green. Compounds with larger size R, such as BaLa$_2$CuO$_5$ and BaNd$_2$CuO$_5$, are brown with a tetragonal P4/mmb structure.

The mercury-containing high T$_c$ superconductor oxides, HgBa$_2$Ca$_{n-1}$Cu$_n$O$_{2n+2+6}$, n=1,2,3,... have received considerable attention in recent years because this family of compounds exhibits the highest T$_c$ values among the known systems to date [7, 8]. In the formula for the homologous series HgBa$_2$Ca$_{n-1}$Cu$_n$O$_{2n+2+6}$, as n goes from 1 to 3, the T$_c$ values increase from 94 K, to 127 K and to 132 K respectively [8]. At high pressure, these compounds exhibit even higher T$_c$ values as well as many unusual properties, including high pressure (P)-induced T$_c$-enhancement [9]. The bulk modulus of HgBa$_2$CuO$_{4+8}$ (Hg-1201) has been predicted to be 83 GPa by Novikov et al. [10], who used total-energy local-density band structure calculation methods. Cornelius and Shilling [11] also calculated the value to be 91 GPa for Ba$_2$HgCuO$_{4+16}$ and 88 GPa for Ba$_2$HgCuO$_{4+11}$ using an empirical model based on comparative crystal chemistry. Hunter et al. [12] measured the compressibility of this material using neutron diffraction with a helium gas compressor and reported a value for the bulk modulus of 69.9 GPa. Because the neutron diffraction experiments were conducted only up to a hydrostatic pressure range of 0.5 GPa, this result may not be truly representative of the bulk modulus of the material. For this reason, an extension of this measurement to higher pressure is desirable. On the other hand, Eggart et al. [13], however, measured the compressibility to 30 GPa and obtained a bulk modulus of 65.4 ± 3 GPa, they used a neon gas pressure medium which did not provide a hydrostatic environment at a pressure of 5 GPa because it became a solid. The reported bulk modulus based on data obtained in nonhydrostatic environments is strongly dependent on the fitting technique. The reported experimental and theoretical values differed by approximately 21 to 28%.

The first goal of this paper is to compare the compressibility and the Young's modulus of the two 121 phases with that of Ba$_2$YCu$_3$O$_{6+x}$ in order to gain insight into the relationship between structure and compressibility, and to the possible role of the 121 phase in improving the mechanical properties of the high T$_c$ sample. The second goal of this paper is to determine the bulk modulus of Ba$_2$HgCuO$_{4+8}$ using x-ray measurements obtained over a hydrostatic pressure range of up to 5 GPa and to compare it with the reported theoretical values. The third goal is to
liquid as the pressure transmitting medium. The inert fluids used in these studies were Fluorinert FC-75* and Dow Corning 200* fluid; both remain hydrostatic to about 5 GPa. The energy dispersive x-ray instrument consists of a solid state detector, a tungsten radiation source and an intrinsic germanium detector which was set at a fixed two theta value for the diffraction studies. A needle-shaped WC collimator with an inside diameter of approximately 0.15 mm was used to guide a narrow x-ray beam towards the sample. Each high pressure x-ray data collection was conducted for a length of 24 to 48 hours. Pressure was measured by the ruby fluorescence method before and after each x-ray measurement.

RESULTS AND DISCUSSION

(1) The 121 phases and Ba$_2$YCu$_5$O$_{6+x}$

The net compressibility of BaNd$_2$CuO$_5$ and BaLu$_2$CuO$_5$ [16] is shown in Figures 1 and 2. In both cases, linear dependence of both the unit cell lattice parameters and volume as a function of pressure were found. Over the pressure range from ambient to 8.7 GPa, the tetragonal unit cell volume of BaNd$_2$CuO$_5$ decreased 5.3%, the cell parameter a decreased 1.8%, and c decreased 1.7%.

![Fig. 1. The pressure dependence of the volume of BaNd$_2$CuO$_5$, showing an envelope of 95% confidence level of the fitted line. Uncertainty bars are the standard uncertainties.](image1)

![Fig. 2. The pressure dependence of the volume of BaLu$_2$CuO$_5$, showing an envelope of 95% confidence level of the fitted line. Uncertainty bars are the standard uncertainties.](image2)
The anisotropic compressibility, $\kappa$, which is defined as the ratio of the $c/a$ compressibility, was thus $1$. This result implies similar packing forces in all three directions. In the BaLu$_2$CuO$_5$ case, a slightly anisotropic compression situation, however, was observed among the three axes. Over the pressure range from ambient to 9 GPa, the orthorhombic unit cell volume decreased 3.8%; both the $a$ and $b$ cell parameters decreased 1.2%; and the $c$ cell parameter exhibited a slightly greater compressibility of 1.5% (anisotropy in the compressibility for both $c/a$ and $c/b$ is 1.25). The respective bulk and Young's moduli for these compounds are: $251 \pm 13$ GPa (combined standard uncertainties from $P$ and $V$ measurements) and $301 \pm 16$ GPa for the green phase, BaLu$_2$CuO$_5$, and $161 \pm 8$ GPa and $193 \pm 9$ GPa for the brown phase, BaNd$_2$CuO$_5$. No pressure-induced phase transformation in either BaNd$_2$CuO$_5$ or BaLu$_2$CuO$_5$ was found.

BaNd$_2$CuO$_5$ consists of a three-dimensional array of edge- and face-sharing BaO$_{10}$ and NdO$_8$ polyhedra [17] (Fig. 3). The NdO$_8$ polyhedron is a trigonal prism capped on two of the three rectangular faces and the BaO$_{10}$ polyhedron is a square prism capped on both ends by tetragonal pyramids. The CuO$_4$ groups alternate with BaO$_{10}$ polyhedron in the $xy$ plane, and with NdO$_8$ layers in the $z$ direction. The similar $a$ and $c$ cell dimensions as well as their compressibility suggest comparable packing strength of the oxide cages along all three dimensions.

Fig. 3. Structure of BaNd$_2$CuO$_5$ [17].

Fig. 4. Structure of BaLu$_2$CuO$_5$ [18].

A review of the structure of the green phase BaLu$_2$CuO$_5$ (Pbnm) [18] as shown in Fig. 4 indicates that all cations in the structure reside in layers which are stacked at 2.8 Å intervals along the $c$-axis. The framework can be considered as built up from distorted monocapped trigonal prisms, LuO$_7$ blocks. Consecutive layers in the $c$-direction are displaced as shown and the Lu prisms are stacked with shared edges to form wave-like chains parallel to the long $b$-axis. The projection of the Lu$_2$O$_{11}$ blocks at $z=1/4$ is shown in Fig. 4 as solid lines, and the second layer at $z=3/4$ is represented as dotted lines. Chains are cross-linked by Cu atoms and by Ba atoms. The compressibility result indicates that it is more difficult to compress the wave-like chains in either the $b$-direction to make them more curvy or the $a$-direction to straighten them, than to compress in the $c$-direction, which is the shortest axis. This is also the direction in which layers of prisms are...
stacked parallel to each other, and presumably is easier to compress. The cage structure in the BaNd$_2$CuO$_5$ compound and wave-like prism chains in BaLu$_2$CuO$_5$ were preserved without collapsing in the pressure range studied.

The high T$_c$ superconductor Ba$_2$YCu$_3$O$_7$ also shows an anisotropic compression feature. The structure which has been studied extensively [19] has perovskite-like CuO layers and chains running perpendicular to the c-direction. The largest compression occurred perpendicular to these CuO layers (2.3%). The least compression was found to occur within the perovskite-like layers because of the oxygen packing (2% in a-direction (oxygen absent in the basal plane [19]) and 1.1% in b-direction (Cu-O chain direction)). The compressibility behavior of Ba$_2$YCu$_3$O$_7$ is similar to the green phase, in which greater compression occurs perpendicular to the layer direction. Figure 5 shows the compressibility curve of Ba$_2$YCu$_3$O$_7$. No phase transformation was observed.

![Graph showing the pressure dependence of the volume of Ba$_2$YCu$_3$O$_7$.](image)

Fig. 5. The pressure dependence of the volume of Ba$_2$YCu$_3$O$_7$.

Currently, there is still disagreement concerning the bulk modulus of Ba$_2$YCu$_3$O$_7$. Reported values vary between 55 GPa and 196 GPa [19-24]. The discrepancy in these values could be due to the different measurement techniques employed or to inherent differences in the samples studied, and on how well the ceramic piece was fabricated. The bulk modulus of the green phase type, BaLu$_2$CuO$_5$, from this work is significantly greater than that of BaY$_2$Cu$_3$O$_7$ and the brown phase, BaNd$_2$CuO$_5$. The value of 161 GPa for BaNd$_2$CuO$_5$ obtained in the present study is between these reported values. Therefore, it is difficult to draw a conclusion as to whether BaNd$_2$CuO$_5$ has a higher or lower bulk modulus than Ba$_2$YCu$_3$O$_{6+x}$. It is conceivable that mixing the high T$_c$ phase with the green phase which has a much higher bulk modulus value, i.e., in fiber form, may result in improved mechanical properties of the resulting material.
(2) HgBa$_2$CuO$_{4+\delta}$

The net compressibility of $a$, $c$ and $V$ of HgBa$_2$CuO$_{4+\delta}$ also shows linear dependence on P [25]. Fig. 6 shows the compressibility of $V$ against $P$. No pressure-induced phase transformation was observed. Over the pressure range of ambient to 5 GPa, the compressibility for the $a$ and $c$ axes was found to be 3.42 and 3.96 respectively, yielding an anisotropy ($c/a$) of 1.16. The $a$ cell parameter shrinks by 1.6% as compared to 2.0% for the $c$ parameter over this range of pressure, and the volume shrinks by 5%.

The compressibility behavior of HgBa$_2$CuO$_{4+\delta}$ is similar to the Bi-containing, Tl-containing, and Ba$_2$YCu$_3$O$_{6+\delta}$ type high $T_c$ compounds in that the $c$-axes are more compressible than the $a$- and $b$-axes. The anisotropy of a few selected Bi-, Tl- and Hg-superconductors are also listed in Table 1. Because the high $T_c$ Bi- and Tl-containing compounds all have perovskite-like layered structures, the least compression direction is expected to occur within these layers (weaker forces), and the larger compression occurs perpendicular to these layers.

![Fig. 6. The pressure dependence of the volume of HgBa$_2$CuO$_{4+\delta}$, showing an envelope of 95% confidence level of the fitted lines. Uncertainty bars show the standard uncertainties.](image1)

![Fig. 7. Structure of HgBa$_2$CuO$_{4+\delta}$](image2)

The unit cell contains two apical Cu-O bonds and two Hg-O bonds which make up the interlayered CuO$_2$ plane spacing along the $c$ direction [26, 12] (Fig. 7). The apical Cu-O(2) distances, 2.786(3)Å, are exceptionally long as compared to the in-plane Cu-O(1) distance of 1.94025(4)Å, and one would expect this bond to be highly compressible. Hunter et al. [12] have performed in situ high pressure Rietveld refinements and have
computed the compressibility of $\kappa_{\text{CuO}_2}$, and $\kappa_{\text{HgO}_2}$ along the c-axis. They found that the $\kappa_{\text{CuO}_2}$ value, $9(3)$, is much higher than that of $\kappa_{\text{HgO}_2}$, $1(4)$, indicating that the Hg-O bond is relatively stiff.

The bulk modulus of this 1201 phase was estimated to be $94.7 \pm 4.2$ GPa and the Young's modulus, \( Y \), $170 \pm 8$ GPa (standard uncertainties). This bulk modulus value, while it differs by 24\% from that measured by Hunter et al. [12] ($69.9 \pm 0.5$ GPa) and 29\% from that by Eggart et al. [13] ($65.4 \pm 3$ GPa), compares reasonably well with Cornelius and Shilling's values of 91 GPa (1.8\% difference), and 88 GPa (5.0\% difference) [11], and reasonably well with Novikov et al.'s value of 83 GPa (10.4\% difference) [10].

Table 1. Compressibility anisotropy of selected compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Anisotropy</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{BaNd}_2\text{CuO}_5$</td>
<td>$0.94 \pm 0.07$</td>
<td>Wong-Ng et al. [16]</td>
</tr>
<tr>
<td>$\text{BaLu}_2\text{CuO}_5$</td>
<td>$1.25 \pm 0.08$</td>
<td>Wong-Ng et al. [16]</td>
</tr>
<tr>
<td></td>
<td>$1.25 \pm 0.12$</td>
<td></td>
</tr>
<tr>
<td>$\text{Ba}<em>2\text{YC}</em>{u3}\text{O}_{6.98}$</td>
<td>$1.2 \pm 0.30$</td>
<td>Block et al. [24]</td>
</tr>
<tr>
<td></td>
<td>$2.1 \pm 0.30$</td>
<td></td>
</tr>
<tr>
<td>$\text{Ba}<em>2\text{YC}</em>{u3}\text{O}_{6.93}$</td>
<td>$1.9$, $2.6$</td>
<td>Jorgensen et al. [21]</td>
</tr>
<tr>
<td>$\text{Ba}<em>3\text{YC}</em>{u3}\text{O}_{6.6n}$</td>
<td>$1.7$, $1.9$</td>
<td>Jorgensen et al. [21]</td>
</tr>
<tr>
<td>$\text{Tl-1212}$</td>
<td>$1.42$</td>
<td>Hunter et al. [12]</td>
</tr>
<tr>
<td>$\text{Tl-2223}$</td>
<td>$2.2$</td>
<td>Schilling and Klotz [27]</td>
</tr>
<tr>
<td>$\text{Hg-1201}$</td>
<td>$1.16 \pm 0.11$</td>
<td>Gonzalez [25]</td>
</tr>
<tr>
<td>$\text{Hg-1212}$</td>
<td>$2.05$</td>
<td>Hunter et al. [12]</td>
</tr>
<tr>
<td>$\text{Hg-1223}$</td>
<td>$2.18$</td>
<td>Gao et al. [28]</td>
</tr>
<tr>
<td>$\text{Bi-2212}$</td>
<td>$2.8$</td>
<td>Olsen et al. [29]</td>
</tr>
</tbody>
</table>

**SUMMARY**

While linear compressions of the unit cell parameters of $\text{BaNd}_2\text{CuO}_5$ exhibit isotropic compressive behavior within our experimental error, $\text{BaLu}_2\text{CuO}_5$ shows anisotropic compressibility (Table 1) which can be explained by the wave-like packing behavior of the LuO$_7$ prisms. No pressure-induced phase transformation in either $\text{BaNd}_2\text{CuO}_5$ or $\text{BaLu}_2\text{CuO}_5$ was found. The cage structure in the $\text{BaNd}_2\text{CuO}_5$ compound and wave-like prism chains in $\text{BaLu}_2\text{CuO}_5$ were preserved without collapsing in the pressure range studied. The bulk modulus of $\text{BaLu}_2\text{CuO}_5$ ($251 \pm 13$ GPa) determined from this work is significantly greater than that of $\text{BaY}_2\text{Cu}_3\text{O}_7$ (reported values of bulk modulus range from

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55 to 196 GPa) and BaNd$_2$CuO$_5$ (161 ± 8 GPa). Thus, there is a possibility that mixing the high $T_c$ phase with the green phase (i.e. in fiber form) may result in improved toughness value of the material.

The anisotropic compressibility of HgBa$_2$CuO$_4$$_6$ (Hg-1201) follows the first order Bridgman's equation and yields a bulk modulus of 94.7 ± 4.2 GPa and an estimated Young's modulus of 170 ± 8 GPa. The compressibility and bulk modulus calculated in this work agrees well with the calculated values of Cornelius and Schilling [11] and Novikov et al. [10]. No pressure-induced phase transformation was observed in this compound between ambient pressure and 5 GPa.

* Certain trade names and company products are mentioned in the text or identified in illustrations in order to adequately specify the experimental procedure and equipment used. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology.

REFERENCES