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RESISTANCE MEASUREMENTS AT HIGH PRESSURE IN THE SYSTEM $BaPb_{1-x}Bi_xO_3$

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Resistance measurements have been made in the system $BaPb_{1-x}Bi_xO_3$ at pressures of up to ~125 kbar at room temperature. A distinct change in slope of R/R_0 vs P indicates the onset of a transition, possibly to the metallic state, which takes place continuously over a wide range of pressure.

HIGH PRESSURE phase transitions to the metallic state have recently attracted much attention. An excellent review by Jayaraman[1] presents the most important recent work. Of special significance to the present study is the discussion on semiconducting to metallic type transitions that occur discontinuously or continuously as a function of pressure.

The system $BaPb_{1-x}Bi_xO_3$ was recently studied[2] and complete solid solubility between $BaPbO_3$ and $BaBiO_3$ was reported. The compounds $BaPb_{1-x}Bi_xO_3$, where $x \leqslant 0.3$, were black and metallic, and showed superconductivity. For $x > 0.3$ the compounds were bronze-like and semiconducting.

The present investigation was undertaken to see if high pressures would induce metallic conduction for the compounds with $x > 0.3$.

Compounds with various compositions were prepared by pressing the appropriate amount of finely ground oxide (Bi_2O_3, PbO) and carbonate ($BaCO_3$) into a slug and then heating in air at 800–900°C. The process was repeated twice, and X-ray diffraction techniques showed that none of the starting materials was present.

Four-wire and two-wire resistance measurements were performed on finely ground polycrystalline samples having the following compositions $BaPbO_3$, $BaPb_{0.65}Bi_{0.35}O_3$, $BaPb_{0.6}Bi_{0.4}O_3$, $BaPb_{0.5}Bi_{0.5}O_3$ and $BaPb_{0.3}Bi_{0.7}O_3$. Pressure was generated in an opposed anvil device and the sample was either embedded in a pyrophyllite annulus or prepressed into a wafer of the correct diameter. These wafers of samples were made slightly thicker than normal to allow for extrusion under compression. In most cases the samples were of the correct[3] thickness to achieve favourable pressure distribution, as confirmed by post-run measurement of the sample.

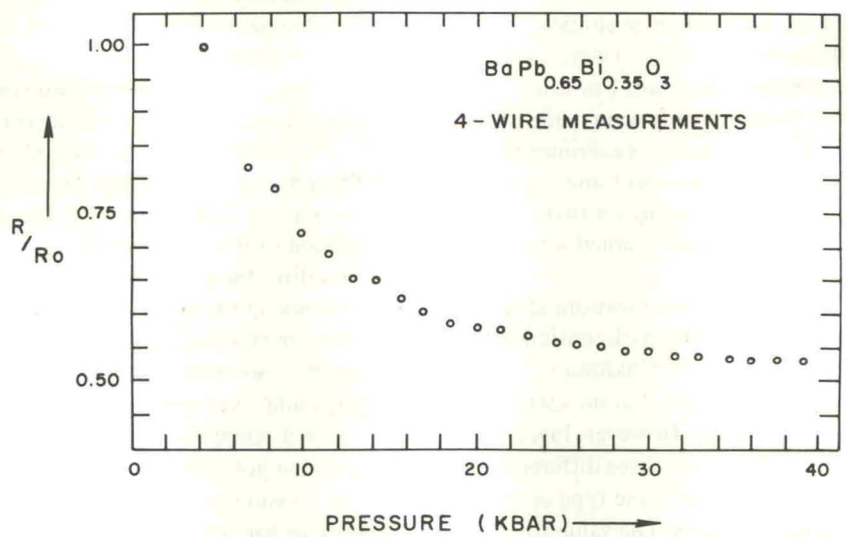

Fig. 1. Results obtained from 4-wire resistance measurements to ~40 kbar on $BaPb_{0.65}Bi_{0.35}O_3$.

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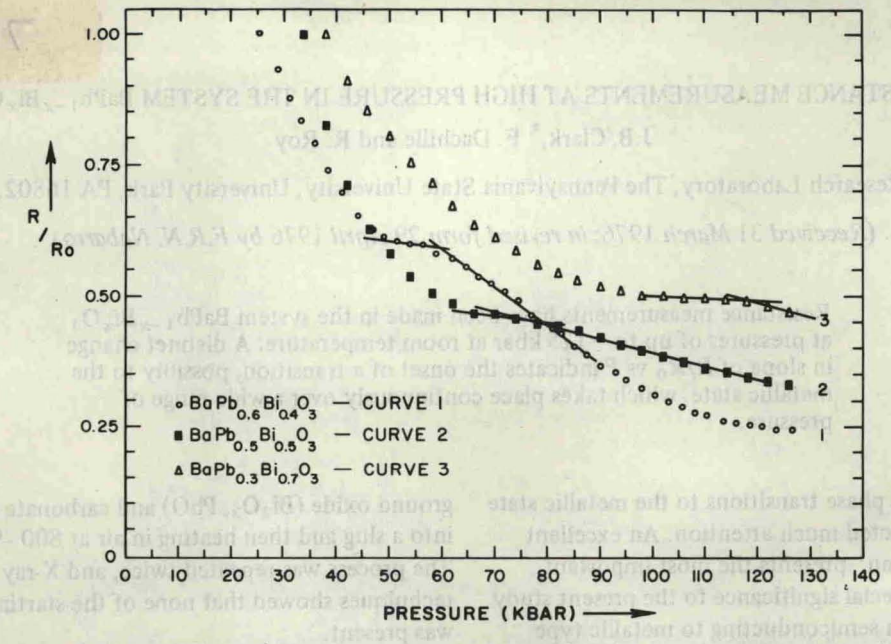

Fig. 2. Results obtained from 2-wire resistance measurements to ~125 kbar on: (1) $BaPb_{0.6}Bi_{0.4}O_3$; (2) $BaPb_{0.5}Bi_{0.5}O_3$; (3) $BaPb_{0.3}Bi_{0.7}O_3$.

Figure 1 shows the results using 4-wire techniques to 40 kbar on a sample of composition $BaPb_{0.65}Bi_{0.35}O_3$. In this work it is difficult to obtain accurate values for the actual resistivity. Therefore the relative resistance R/R_0 (where R_0 = initial resistance in each run) is plotted as a function of pressure. Figure 1 shows a sharp initial drop in the value of R/R_0 with increasing pressure which is primarily due to the initial compaction of the polycrystalline sample. However, no sharp breaks or marked slope changes were detected to a pressure of ~39 kbar.

In order to extend the pressure range studied, smaller faced anvils (diameter = 4.76 mm) were used, making four-wire measurements difficult. For this reason only two-wire resistance measurements were made of the sample-anvil composite. In total, 26 experiments were performed on the compositions mentioned to a variety of maximum pressures depending on anvil performance. The maximum pressure attained was ~125 kbar.

The results obtained from the compositions studied can be summarised as follows: No sharp discontinuous drop in resistance was detected to the maximum pressures studied. This would indicate that no sharp transition to a metallic state occurs. However, Fig. 2 shows the typical results obtained for three different compositions and all curves show the same type of clear slope change at higher pressures. The value for R/R_0 initially drops sharply, then passes through a region where it flattens off only to start dropping sharply again at still higher pressures. In all cases the latter slope change is thought to indicate the onset of a transition. The transition seems to occur over a large range in pressure $\geqslant$ 50 kbar and in most cases is only completed above the maximum pressures attainable in the present work. This can be deduced from Fig. 2 curve 1, where the transition appears to occur at ~59 kbar and seems to be nearing completion above ~115 kbar. The proposed high pressure phase cannot automatically be assumed to be a metallic phase in the absence of data with temperature variation.

Experiments done on metallic $BaPbO_3$ showed that the value obtained for R/R_0 remained essentially unchanged to ~100 kbar.

From Fig. 2 it is possible to estimate (as shown) the onset of the transition at ~59 kbar for $BaPb_{0.6}Bi_{0.4}O_3$, ~76 kbar for $BaPb_{0.5}Bi_{0.5}O_3$ and ~118 kbar for $BaPb_{0.3}Bi_{0.7}O_3$. One might expect a similar transition to occur for $BaBiO_3$ at ~175 kbar by linear extrapolation of the above results versus composition.

To confirm the proposed transitions, resistivity measurements on single crystals would be of great value. Measurements on single crystals would remove all intergranular resistance effects which might be present in polycrystalline samples. Figure 3 shows the results obtained for a sample of $BaPb_{0.5}Bi_{0.5}O_3$ on increasing and decreasing pressure. The slope change found on increasing pressure is also clearly visible on decreasing pressure. This behaviour was also found for other compositions, but a complete set of data is difficult to obtain on increasing and decreasing pressure because of blow-outs occurring. The reproducible nature of the

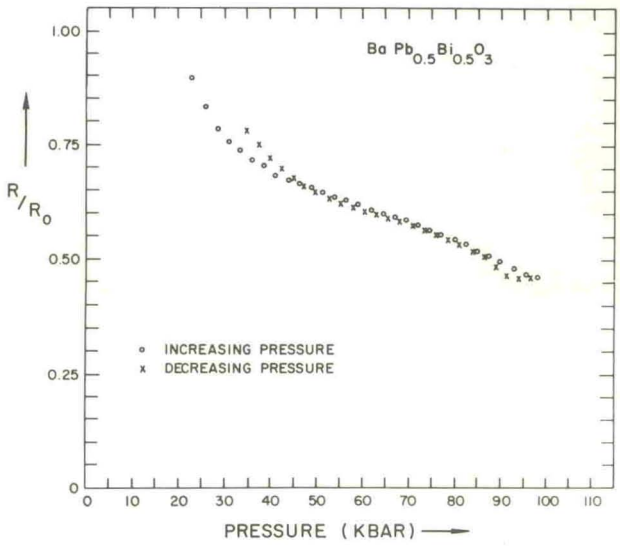

Fig. 3. Results obtained from 2-wire resistance measurements on increasing and decreasing pressure for $BaPb_{0.5}Bi_{0.5}O_3$.

slope change on increasing and decreasing pressure supports the suggestion that it is related to a phase change, as opposed to simple intergranular resistance effects in the polycrystalline sample.

Sleight *et al.*[2] discussed the possible schematic energy level diagram for $BaPbO_3$. They postulated that the 6*s* band would split above $x = 0.35$ in the compounds $BaPb_{1-x}Bi_xO_3$ and thus cause their semiconducting properties. In the light of the above considerations it would seem that the application of sufficient pressure could cause the band gap to close.

The bismuth ions were earlier[4] thought to have the unusual 4+ valency. Such a situation would probably have yielded a metallic $BaBiO_3$. From the latest structural data[5] available for $BaBiO_3$, using X-ray and neutron diffraction techniques, the true valence state appears to be $Ba_2Bi^{3+}Bi^{5+}O_6$. This valence situation would appear to be better suited to the semiconducting properties of the compound.

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