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Preparation and properties of a barium-graphite compound

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A barium-graphite intercalated compound was prepared by vapour diffusion anneal of barium into well oriented pyrolytic graphite. The resulting specimens maintained their integrity and were well oriented along the *c*-axis. The compound reacts with air, but is not as reactive as the corresponding alkali metal intercalates. Chemical analysis indicated that the compound formed had a stoichiometry of about C_8Ba. This, along with the results of X-ray analysis, suggest that the compound has a structure similar to C_8Ma, where Ma is an alkali metal. The compound was shiny gold in colour, brittle, and had a hardness about five times that of pyrolytic graphite. Resistivity and thermoelectric power measurements indicate that the compound is metallic in nature.

1. Introduction

A large number of intercalated graphite compounds have been prepared and studied [1–3]. Among the most thoroughly investigated compounds are those formed by the intercalation of potassium, rubidium and caesium [4–15]. The picture that emerges from these studies is that metal atoms arrange themselves in a two-dimensional array between graphite sheets and that they ionize, at least partially, donating electrons to the conduction band, thereby increasing electrical conductivity.

In view of the fact that the lattice spacing of the alkaline earths are close to those of the alkali metals (Rb and Ba have almost identical atomic sizes) and since the alkaline earths ionize easily, they should form intercalated graphite compounds In fact, compounds of barium and graphite have been prepared and some of their properties determined [16, 17].

In the present study, an intercalated barium compound of graphite was prepared, structural and chemical analysis was performed, and some physical properties measured. The results suggest that the compound has a structure similar to that of the most saturated alkali compounds and has the formula C_8Ba. The compound is bright metallic gold in colour, has a Knoop hardness of 23 and is brittle. It has a *c*-axis resistivity of about 0.034 Ω-cm at room temperature (compared to 0.22 Ω-cm for graphite) which is a linear function of temperature. The compound has a *c*-axis thermoelectric power of $-9\,\mu V°\,C^{-1}$ that is independent of temperature.

2. Compound preparation

The compound was prepared by heating well-oriented pyrolytic graphite (courtesy of the General Electric Metallurgical Division) and 99.95% pure barium together in a furnace. The specimens were cubes with sides of about 1 cm. These materials were contained in a specially designed stainless steel crucible enclosed in a vycor capsule, which was evacuated to 2×10^{-5} Torr and sealed before the heating. Speed and care is necessary in handling the barium and cleaning its surface, since it reacts readily with air.

Barium forms a carbide with carbon, so that it was necessary to determine an optimum time–temperature heat-treatment which maximized the formation of intercalated compound and minimized carbide formation. This was found to be 400h at 575° C. Above this temperature, barium

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carbide started to form, and below it, the diffusion anneal took too long to give significant amounts of intercalated compound. The presence of carbide was detected visually and by X-ray measurements.

As a result of the heat-treatment, the barium diffused into the graphite, which doubled in size in the *c*-direction while remaining virtually unchanged in the *a*-direction. The final specimens consisted of shiny golden compound surrounding a soft black core. The compound extended about 0.25 cm into the specimen, i.e. more than half the material was compound. Samples for analysis and physical properties measurements were cut from the shiny gold coloured parts of the specimen.

The intercalated compound reacts in air and begins to darken in 10 sec after exposure. Bulk reaction is relatively slow: after 24h exposure to dry air, splitting the specimen to expose new *c*-faces restored the surfaces to the original colour.

3. Chemical analysis

Analysis for barium in the barium-graphite compound was performed by Galbraith Laboratories of Knoxville, Tennessee by a barium sulphate precipitation method estimated to be accurate to 0.5%. The average of four specimens prepared at 575° C yielded the stoichiometry $C_{7.4}Ba$.

Analysis for barium carbide was carried out by reacting the barium-graphite compound with water, collecting any gas formed, and analysing it for acetylene in a mass spectrometer. The amount of barium carbide was below the limits of X-ray detection for specimens formed at 575° C. A specimen prepared at 635° C was analysed by the acetylene method and contained 2.7% by weight of barium carbide.

It should be noted that Guérard and Herold [16] reported the synthesis of a barium-graphite intercalation compound with the formula C_6Ba. Although they note the presence of barium carbide in their specimens, the time–temperature data describing the specimen preparation was not reported, and it is not clear to what extent the presence of carbide was taken into account in their analysis.

4. Debye–Scherrer measurements

The original pyrolytic graphite, the gold coloured intercalated compound, the soft black core material in the diffusion annealed specimens, and the grey material believed to be barium carbide, were all subjected to Debye–Scherrer analysis. The grey material was found to have spacings in agreement with reported data for barium carbide [16]. The original pyrolytic graphite was found to have lattice parameters $c = 6.69$ Å and $a = 2.46$ Å, while the black core material had values of $c = 6.70$ Å and $a = 2.47$ Å. These are in close agreement with the accepted values for graphite [17]. The gold coloured intercalated compound had parameters $c = 5.28$ Å and $a = 2.49$ Å. The *c* value in this case is interpreted to be equal to the closest distance between graphite layers, whereas in graphite, *c* is twice this distance. The reason for this is that the macroscopic length in the *c*-direction nearly doubles upon intercalation, and it is known that in the alkali metal intercalates, the stacking sequence of graphite --- ABA --- converts to the sequence --- AMA --- upon intercalation where M represents a layer of metal [8].

The expansion of the carbon–carbon bond length as indicated by the 0.02 Å difference in *a*-spacing between graphite and compound is consistent with the results of Nixon and Parry [18] who found a similar effect for potassium-graphite.

The spacings determined by us are in reasonable agreement with those determined by Guérard and Herold [16].

5. Microhardness

Measurements of microhardness were made along a cross-section perpendicular to the *c*-axis. The measurements were performed with a Wilson Tukon tester using a Knoop indenter with a 200g load. The results are given in Table I. The compound is more than five times harder than the pyrolytic graphite for the same orientation, the specimen core has a hardness somewhat less than that of graphite, while the hardness at the interface between the core and the compound has an intermediate value.

The compound is quite brittle, and samples often cracked around the indenter when tested. Also, the tests were performed in air so that some reaction of the compound with the atmosphere took place. The reported measurements were made

TABLE I Results of microhardness measurements

Material	KHN
Barium-graphite	23.1
Interface	13.5
Core	3.8
Graphite	4.5

as rapidly as possible and significant visible deterioration of the sample did not occur. Nevertheless, the accuracy of the values in Table I is not known, and the results are to be regarded as being tentative.

6. Resistivity measurements

The resistivity of the barium-graphite compound along the *c*-axis was determined as a function of temperature from room temperature to 600°C. A specially constructed apparatus using pressure contacts was used that permitted the measurements to be made in a vacuum.*

Measurements of the *c*-axis resistivity of the pyrolytic graphite are shown in Fig. 1. They show the decrease of resistivity with increasing temperature and are in accord with published results for similar materials [21].

The results for the barium graphite compound are shown in Fig. 2. The dotted curve is the result of measurements taken on an initial run as the compound was heated. Imperfect matching of the compound surface with the silver-soldered contacts gave a contact resistance which decreased as the temperature was raised and proper matching was established. The solid line is the result of

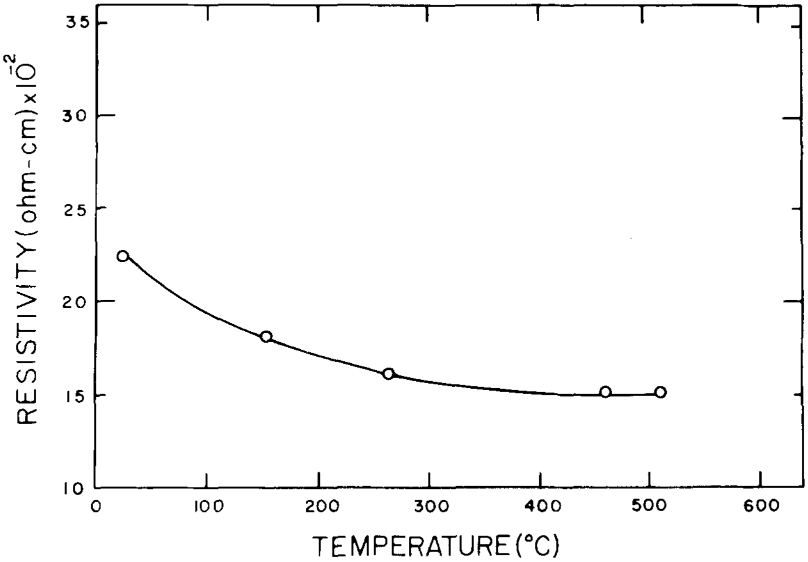

Figure 1 Resistivity of pyrolytic graphite.

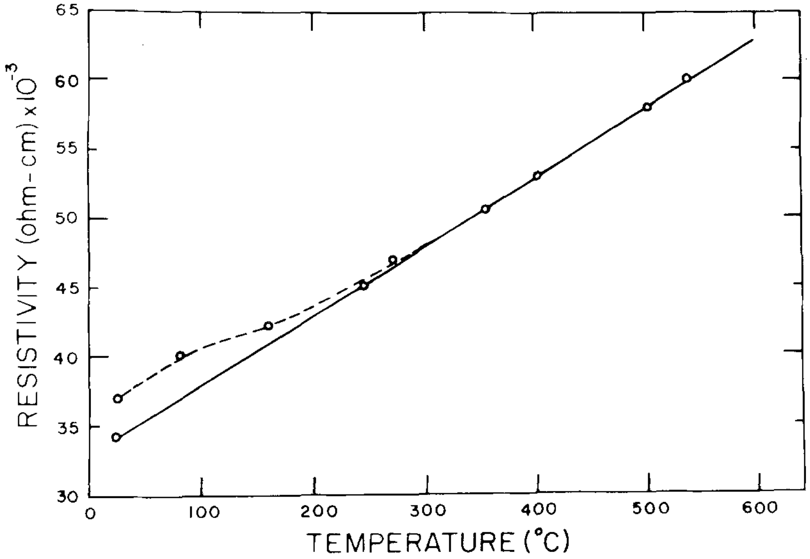

Figure 2 Resistivity of barium graphite compounds.

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* See [17] for the construction of this apparatus, and for the details of other experimental measurements presented in this paper.

measurements made during a cooling cycle. Further heating and cooling cycles followed the solid line.

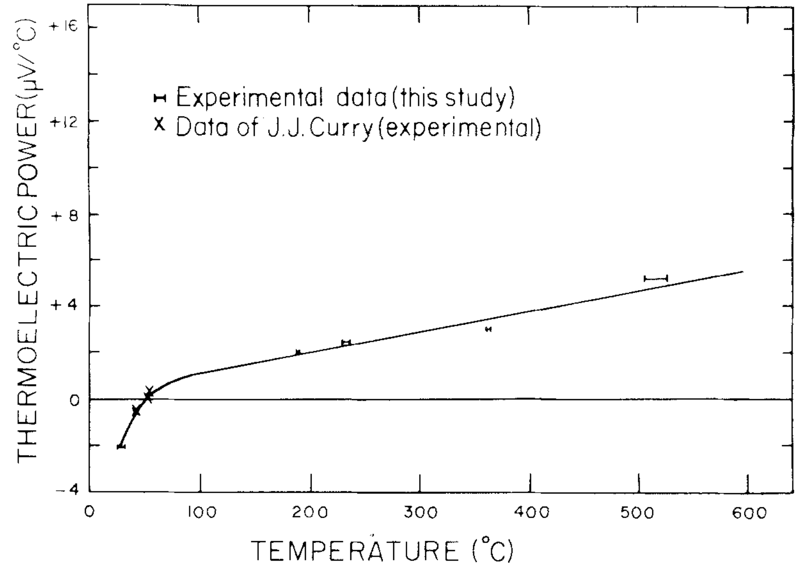
The room temperature c-axis resistivity of the compound was found to be $34 \times 10^{-3} \Omega$-cm, more than an order of magnitude smaller than the corresponding value for the pyrolytic graphite, which was $22 \times 10^{-2} \Omega$-cm. The resistivity of the compound increases linearly with temperature, indicating metallic behaviour.

7. Thermoelectric power measurements

Thermoelectric power along the c-direction was measured in an apparatus which was a slight modification of that used by Curry [22]. Fig. 3 shows the results for the pyrolytic graphite. Values near the zero of thermoelectric power, indicated by crosses, were obtained by Curry. The room-temperature value is $-2 \mu V\,°C^{-1}$ which increases and then becomes positive as the temperature increases, indicating a transition from N type to P type behaviour.

The thermoelectric power for the barium graphite compound along the c-direction is shown in Fig. 4. It has a value of $-9 \mu V\,°C^{-1}$ which is independent of temperature, indicating metallic behaviour.

Figure 3 Thermoelectric power of pyrolytic graphite.



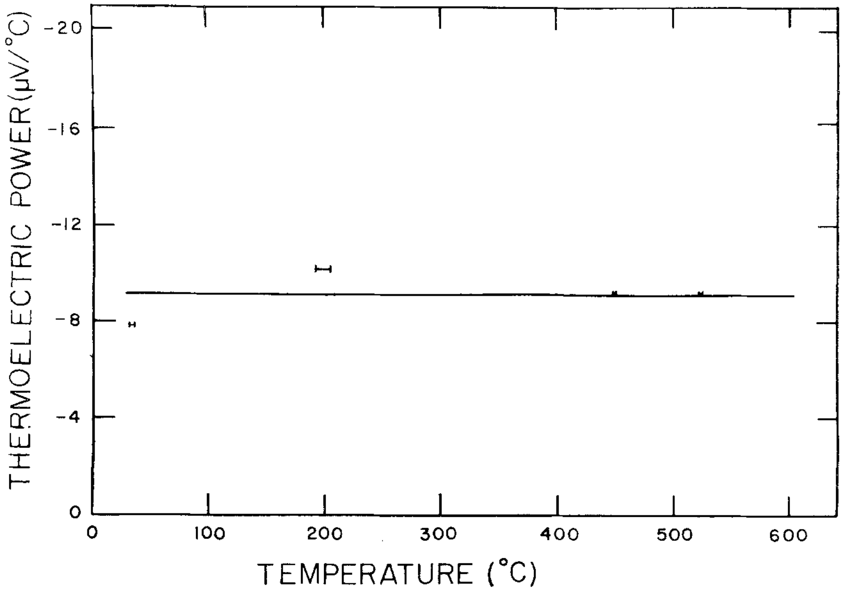


Figure 4 Thermoelectric power of barium graphite compounds.

8. Conclusion

A barium-graphite intercalated compound was prepared by vapour diffusion anneal of barium into well oriented pyrolytic graphite. The resulting specimens maintained their integrity and were well oriented along the *c*-axis. The compound reacts with air, but is not as reactive as the corresponding alkali metal intercalates.

Chemical analysis indicated that the compound formed had a stoichiometry of about C_8Ba. This, along with the results of X-ray analysis, suggests that the compound is a first stage compound similar to C_8Ma, where Ma is an alkali metal.

The compound was shiny gold in colour, brittle and had a hardness about five times that of pyrolytic graphite.

Resistivity and thermoelectric power measurements indicate that the compound is metallic in nature.

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