Reprinted from

SOLID STATE COMMUNICATIONS

A PHASE TRANSFORMATION IN LEAD–BISMUTH ALLOYS INDUCED BY HIGH PRESSURE

D.E. Gordon and B.C. Deaton

Applied Research Laboratory, General Dynamics, Fort Worth Division,
Fort Worth, Texas, U.S.A. 76101

High-pressure experiments on Bi–Pb alloys are reported. X-ray diffraction results show that the high-pressure modification (at 16 kbar) of a Bi–Pb alloy formed at a composition of approximately 37 at.% lead has a double hexagonal close-packed (La-type) structure. Electrical resistivity and specific volume discontinuities were observed at the transformation pressure.

THE DOUBLE hexagonal close-packed (d.h.c.p.) crystal structure was first reported in the rare earths and their alloys. However, more recently the d.h.c.p. structure has been found in Mg, Ag–In, and Ag–Sb alloys under high pressure[1] and in the Au–In[2] and Au–Ga[3] alloy systems at normal pressure. This paper describes the formation of a d.h.c.p. phase in the Bi–Pb alloy system under pressure.

Bridgman[4] first reported the formation of an irreversible phase in the Bi–Pb system after exposure to pressures of 10 kbar or more, centering around 37 at.% lead with a narrow range of homogeneity. However, due to the extreme sluggishness of this phase transition, it is doubtful whether equilibrium was attained in these investigations. The phase diagram of the Bi–Pb system has been widely investigated at atmospheric pressure.[5] Across the phase diagram, the system consists of three phase fields: (i) alpha, the rhombohedral Bi-rich solid solution; (ii) beta, the hexagonal close-packed intermediate phase centering around 30 at.% bismuth, believed to have a crystal structure closely related to the high-pressure polymorph of lead,[6] and (iii) gamma, the face-centered cubic Pb-rich solid solution. The range of the Bi-rich solid solution, alpha, is only 1 or 2 at.% Pb. The beta single-phase region extends from approximately 25–32 at.% Bi.

The composition limits of gamma range from 100 to approximately 80 at.% Pb. At a composition of 37 at.% Pb, where the high-pressure phase is formed, the alloy consists of a mixture of the alpha and beta phases at atmospheric pressure.

The bismuth and lead used were 99.999 + % purity and were purchased from the American Smelting and Refining Company. The high-pressure phase was identified by employing an opposed diamond-anvil (Materials Research Corporation Model XKB-100) high-pressure apparatus similar to that described by Piermarini and Weir.[7] This device is a pneumatic loading cell capable of producing pressures up to approximately 100 kbar on materials under X-ray investigation. Gas pressure is admitted behind a sliding piston over an area 2 in. dia. This force is concentrated on a nominal 0.020 in. dia. flat polished on the end of the piston diamond. $M_0 K\alpha$ radiation was used.

Compressibility measurements were performed using a piston-cylinder apparatus described previously.[8] Resistance measurements were made with a tetrahedral anvil device also described in an earlier paper.[9] Pressures are believed to be accurate to within ± 1.0 kbar on the compressibility and resistance measurements.
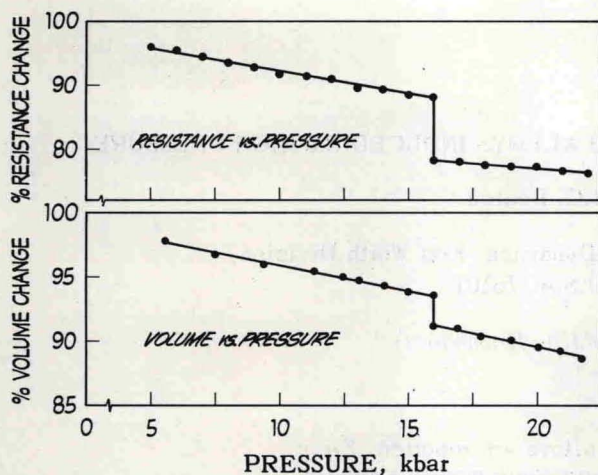
FIG. 1. Change in resistance and volume with pressure for Bi $_{0.625}$ Pb $_{0.375}$ sample.

Table 1. X-ray data on the high-pressure phase of Bi $_{0.625}$ Pb $_{0.375}$ at 20 kbar.

hkl	d_{obs}	d_{calc}	I_{obs}
100	2.97	2.980	MW
101	2.88	2.882	S
004	2.82	2.820	M
102	2.64	2.642	VS
103	2.35	2.348	M
104	2.03	2.042	M
105	1.83	1.816	W
110	1.71	1.695	MW
106	1.59	1.594	M
201	1.46	1.472	
114	(broad)	1.470	M
202		1.452	
107	1.41	1.415	
008	(broad)	1.410	MW

Table 1 lists observed and calculated d spacings for the high-pressure modification at the particular composition Bi $_{0.625}$ Pb $_{0.375}$. The pattern was indexed on a double hexagonal unit cell with $a = 3.45 Å$, $c = 11.30 Å$, and $c/a = 3.28$ at 20 kbar. The density calculated from X-ray data is $11.82 g/cm^3$ for the d.h.c.p. phase. The phase transformation was very sluggish, requiring approximately 2 hr for conversion at 16 kbar. At higher pressures the conversion was somewhat faster.

The transformation to the d.h.c.p. phase was also observed by resistivity and volume discontinuities at 16 kbar. The results of compressibility and resistance measurements for a Bi $_{0.625}$ Pb $_{0.375}$ sample as a function of the sample pressure are shown in Fig. 1. The resistance change is a more sensitive indicator of the formation of the high-pressure phase than is the volume change. The total resistance decrease due to the transformation is 9.9%, while the total volume decrease is 2.4%. The relative volume of the d.h.c.p. structure at 20 kbar compared to 1 bar at 25 °C is 91.2%. Bridgman's[5] compressibility results give a relative volume of 90.4% for the high-pressure phase. The density of the high-pressure phase at 20 kbar, based on our compressibility results, yields a value $\rho = 11.78 g/cm^3$. This result agrees quite favorably with the theoretical density ($\rho = 11.82 g/cm^3$) based on unit cell dimensions.

The Bi$_{\sim 0.3}$ Pb$_{\sim 0.7}$ + Bi $\xrightarrow{16 kbar}$ Bi$_{\sim 0.625}$ Pb$_{\sim 0.375}$ transformation exhibits quite high hysteresis with pressure. A fraction of the d.h.c.p. phase can be retained after release of pressure if the sample is kept at 77 °K.[10] Upon warming to room temperature, all of the high-pressure phase reverts back to the original two-phase mixture.

The high-pressure phase has a narrow range of homogeneity. This is characteristic of the d.h.c.p. phase found in the Au—In alloy system.[2] X-ray diffraction and compressibility results indicate a stability range from ~ 60 to ~ 64 at.% Bi for the single-phase d.h.c.p. structure.

The c/a ratio found for the high-pressure phase is close to ideal[*], as is often found in other d.h.c.p. structures. Why this should be so is not at present clear. Hodges[11] has derived a formula for the deviation in axial ratio from ideal for various close-packed structures. At a transition

---

[*] The ideal c/a ratio for the d.h.c.p. structure is $2 \times 1.633 = 3.266$ based on the stacking of rigid spheres.

between the h.c.p. phase and the d.h.c.p. phase

$$\frac{(c/2a)\,\text{d.h.c.p.} - (c/a)\,\text{ideal}}{(c/a)\,\text{h.c.p.} - (c/a)\,\text{ideal}} = 0.5 \quad (1)$$

according to theory.

In the Bi–Pb alloy system, the c/a ratio of the h.c.p. intermediate phase centering around 30 at.% Bi is 1.65 at the transformation pressure. For the d.h.c.p. phase, $(c/a)/2 = 1.64$ upon formation. Substituting these values into (1), the ratio 0.41 is obtained, which is slightly smaller than the theoretical ratio, 0.5.

The d.h.c.p. structure may be regarded as a structure intermediate between the face-centered cubic and close-packed hexagonal arrangements. The stacking sequence for the d.h.c.p. structure is ABACABACABACA. For this stacking arrangement to hold, the number of f.c.c. structures must equal the number of h.c.p. structures. In the composition range in which the d.h.c.p. structure is formed under pressure, the alloy contains approximately equal proportions of α and β before transformation. If the bismuth present (α phase) transforms to f.c.c. packing under pressure, then the two-phase alloy would contain approximately equal amounts of f.c.c. and h.c.p. phases. Then an intermediate phase such as d.h.c.p. is energetically possible in this composition range. Klement et al. [12] have proposed that the structure of BiV could be f.c.c. in analogy with the high-pressure phase in thallium. The vol/atom of the d.h.c.p. structure immediately upon formation is $29.8\,\text{Å}^3$. The vol/atom of Bi III upon formation is $30.2\,\text{Å}^3$. Due to the relatively small energy difference between Bi III and Bi V ($\Delta V = 1.2\%$ upon formation of Bi V from Bi III), it is conceivable that the bismuth (α phase) present in the $\text{Bi}_{0.625}\text{Pb}_{0.375}$ sample transforms to Bi V in order to form the intermediate d.h.c.p. phase at high pressure.

REFERENCES

1. PEREZ-ALBUERNE E.A., CLENDENEN R.L., LYNCH R.W. and DRIKAMER H.G., *Phys. Rev.* A142, 392 (1966).

2. HISCOCKS S.E.R. and HUME-ROTHERY W., *Proc. R. Soc.* 282, 318 (1964).

3. COOKE C.J. and HUME-ROTHERY W., *J. less-common Metals* 10, 42 (1966).

4. BRIDGMAN P.W., *Collected Experimental Papers* Vol. VII, pp. 4451–4468, Harvard University Press, Cambridge, Mass. (1964).

5. HANSEN M., *Constitution of Binary Alloys* pp. 324–326, McGraw-Hill, New York (1958).

6. KLEMENT W., Jr., *J. chem. Phys.* 38, 298 (1963).

7. PIERMARINI G.J. and WEIR C.F., *J. natn. Bur. Stand.* 66A, 325 (1962).

8. WARD K.B., Jr. and DEATON B.C., *Phys. Rev.* 153A, 947 (1967).

9. BLUM F.A., Jr. and DEATON B.C., *Phys. Rev.* 137A, 1410 (1965).

10. GORDON D.E. and DEATON B.C., *Phys. Lett.* 27A, 116 (1968).

11. HODGES C.H., *Acta Metall.* 15, 1787 (1967).

12. KLEMENT W. Jr., JAYARAMAN A. and KENNEDY G.C., *Phys. Rev.* 131, 632 (1963).

Nous présentons des expériences à hautes pressions sur des alliages de Bi–Pb. Les résultats de la diffraction par rayons X montre que la modification à haute pression (16 kbar) d'un alliage de Bi–Pb, ayant approximativement 37% de plomb atomique, est une structure double-hexagonal serrée (type La). Des discontinuités dans la résistivité électrique et le volume spécifique ont été observé durant la transformation.