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Polymorphic transition of $GaNbO_4$ under high pressures

The crystal structure of $GaNbO_4$ under atmospheric pressure was studied by Morosin and Rosenzweig [1] and found to be $AlNbO_4$-like with a non-centric space group C2 ($a = 12.660$, $b = 3.7921$, $c = 6.6147$ Å, $\beta = 107.90°$ and $Z = 4$ unit formulae/cell). The co-ordination about gallium and niobium is a highly distorted octahedral one. The idealized structure of $GaNbO_4$ at standard pressure is shown in Fig. 1.

A hexahedral anvil type apparatus and a piston–cylinder type apparatus were used for generating pressure ranging over 7 to 50 kbar, and an internal heating type apparatus using the argon gas was used for generating pressure ranging over 1 to 1.5 kbar.

A mixture of Nb_2O_5 ("spectrographically standardized", chemical analysis in the previous paper [2]) and Ga_2O_3 (99.999% pure) was sealed in a platinum capsule to prevent reduction. The procedures for the runs were given in the previous paper [2], when the piston–cylinder and hexahedral anvil type apparatuses were used. When the internal heating type apparatus using argon gas was used, the samples were quenched at a rate of approximately 60° C min^{-1} before the pressure was released. After the run, each sample, was analysed by X-ray diffraction, using nickel-filtered copper radiation.

The X-ray powder patterns are shown in Table I, which indicates that the high-pressure structure is very likely of the wolframite type (Fig. 1) that

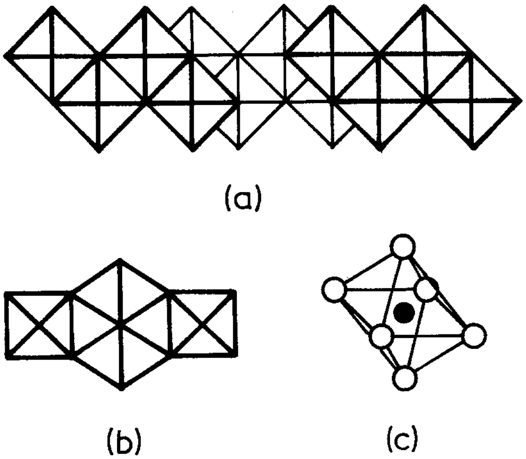

Figure 1 (a) The idealized structure of $GaNbO_4$ at standard pressure; each square represents an octahedron in projection as viewed from a corner, the lighter lines indicate displacement downwards by half an octahedral diagonal. (b) The idealized structure of wolframite type. (c) Each octahedron consists of oxygen ions at the corners and a metal ion at the centre.

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TABLE I Indexing of the high-pressure form of $GaNbO_4$ (wolframite type)

$h\,k\,l$	d_0	I/I_i	d_c
1 0 0	4.59(5)	5	4.60(6)
0 1 1	3.69(7)	5	3.70(4)
1 1 0	3.54(2)	65	3.55(5)
−1 1 1	2.89(3)	100	2.89(7)
1 1 1	2.87(0)	90	2.87(5)
0 2 0	2.78(2)	15	2.79(5)
0 0 2	2.47(4)	30	2.47(2)
0 2 1	2.42(6)	25	2.43(3)
2 0 0	2.29(8)	20	2.30(3)
−1 0 2	2.16(7)	10	2.18(8)
1 0 2	2.15(2)	15	2.16(9)
−1 1 2	2.03(8)	10	2.03(7)
1 1 2	2.02(0)	10	2.02(2)
0 2 2	1.84(9)	15	1.85(2)
2 2 0	1.77(3)	10	1.77(7)
1 3 0	1.72(1)	25	1.72(7)

appears in $FeNbO_3$ [3,4], and the lines are indexed on the basis of a monoclinic unit cell, $a = 4.60(6)$, $b = 5.59(0)$, $c = 4.95(5)$ Å, $\beta = 90.5(8)°$, $V = 127.\ (3)$ Å^3 and $Z = 2$ unit formulae/cell. The packing parameter, V_i/V_u, where V_i is the sum of ionic volumes per unit formulae and V_u the crystalline volume per unit chemical formula, is 0.636 for the $AlNbO_4$ type (from Morosin's lattice constants) and 0.755 for the wolframite type. The wolframite type was obtained above several kbar (Fig. 2). The boundary of the two phases was not so clear that it might be expressed by a function of pressure and temperature as shown in Fig. 3.

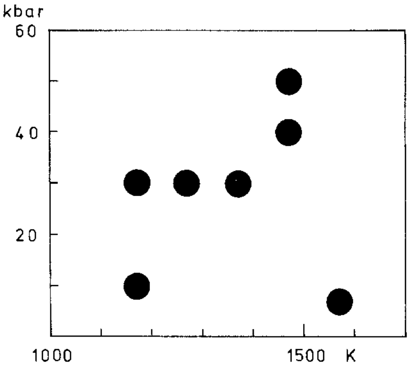

Figure 2 The temperature–pressure phase diagram of $GaNbO_4$ obtained by a hexahedral anvil type apparatus and a piston–cylinder type apparatus.

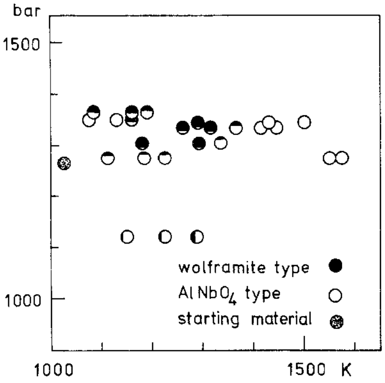

Figure 3 The temperature–pressure phase diagram of $GaNbO_4$ obtained by an internal heating type apparatus using argon gas.

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