

ON THE BRASS- AND SILVER-COLORED FORMS OF PtGa_2

B. MOROSIN*, D. SWENSON**

* Sandia National Laboratories, Org. 1153, MS 1421, Albuquerque, NM 87185-1421

** Materials Science Program, University of Wisconsin, 1509 University Avenue, Madison, WI 53706; currently at Department of Metallurgical and Materials Engineering, Michigan Technological University, 1400 Townsend Drive, Houghton, MI 49931-1295

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ABSTRACT

PtGa_2 has previously been reported to exist as both a brass-colored, fluorite-structured phase and as a silver-colored alloy of unknown crystal structure. The crystal structure of the silver-colored form is reported here, along with a discussion of the stoichiometric factors responsible for the polymorphy of this phase. The silver-colored form belongs to the space group $I4_1/acd$, with the lattice parameters $a = 8.5544(4)$ and $c = 21.574(17)$ Å, and $Z = 32$. The structure consists of layers of Pt and Ga stacked along the c axis, in which two crystallographically different Pt and Ga atoms have similar environments involving eight and nine nearest neighbors, respectively. This structural arrangement may be the prototype for a family of ternary platinum metal-Group B-based phases. The present investigation also necessitates changes in the currently accepted Ga-Pt phase diagram. Stoichiometric PtGa_2 undergoes a structural transformation upon cooling from a brass-colored fluorite structure to this silver-colored, tetragonal structure. However, the transformation is inhibited if the composition of the fluorite-structured phase is Ga-poor.

INTRODUCTION

Many of the intermetallic compounds possessing the fluorite (CaF_2 , $Fm\bar{3}m$, CI) structure were first synthesized in the 1930's by Zintl et al. [1], who noted that the phases exhibited a striking variety of colors, ranging from violet (AuAl_2) to copper (PtIn_2) to brass (PtAl_2 , PtGa_2). Such unusual characteristics prompted much additional work to characterize both their physical properties and phase equilibria with, in the case of PtGa_2 , continued confusion existing as to its phase stability at low to moderate temperatures [2].

Zintl et al. [1] noted that PtGa_2 possessed the fluorite structure only at high temperatures; upon slowly cooling brass-colored PtGa_2 from 200 °C to room temperature, it suddenly turned "white" at about 150 °C. X-ray diffraction patterns of this slowly cooled alloy were described as being complicated. The changes in color and X-ray diffraction pattern were found to be reversible upon heating the sample above 150 °C, and moreover it was demonstrated that the fluorite structure could be retained at room temperature by rapidly quenching a powdered sample from 200 °C. This behavior suggests a polymorphic transformation of PtGa_2 near 150 °C. However, several other investigators concluded that PtGa_2 decomposed eutectoidally at 153 °C into Pt_3Ga_7 and Pt_2Ga_3 [3].

Several recent investigators have not found PtGa_2 to show any tendency toward a structural transformation or decomposition at low temperatures. Most notable among these is Baughman, who grew large boules of PtGa_2 using the Bridgman method and reported no difficulties in retaining them in their brass-colored states at room temperature [4]. At the time of their fabrication, one of the present investigators (B.M.) conducted various unpublished single crystal diffraction experiments on sections of these boules without noting any changes in sample color or X-ray diffraction pattern upon cooling from room temperature to approximately 10 K. Moreover, large portions of these boules are in the possession of the present investigators, and although over 20 years have passed since their fabrication, they have retained their fluorite crystal structure and brass color to this day. Similar long-term, low temperature stability has been observed in the thin films of PtGa_2 grown by other researchers [2].

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Recently, as part of an investigation of phase equilibria in the Ga-In-Pt-As system, one of the present authors (D. S.) prepared alloys with the composition PtGa_2 [2]. Upon quenching in iced water from 875 °C, these alloys changed from brass-colored to silver-colored. An X-ray diffraction pattern of pulverized alloy was found to be very complicated. However, the pattern did not correspond to a combination of Pt_3Ga_7 and Pt_2Ga_3 , as is predicted by the Ga-Pt phase diagram [5], nor did it correspond to that of any of the known platinum gallides. Moreover, pieces of alloy were observed to change reversibly from silver to brass in color when placed on and removed from a 300 °C hot plate. This behavior corresponds rather closely to Zintl et al.'s original observations suggesting a polymorphic transformation of the fluorite phase of PtGa_2 upon cooling. Therefore, the present single crystal X-ray diffraction structural determination of this silver-colored form of PtGa_2 was undertaken. Some additional experiments performed on both the new alloys and on the brass-colored crystals of PtGa_2 grown by Baughman are also reported. While all questions regarding the low temperature stability of fluorite-structured PtGa_2 are not answered, these new data provide insight as to how many of the seemingly disparate observations described above may be made consistent with each other.

EXPERIMENTAL DETAILS

New samples were fabricated from elemental Pt powder of 99.95 at.% purity and Ga ingots of 99.999 at.% purity (both from Johnson Matthey Chemicals, Limited). The elements were weighed in the appropriate ratios for the composition PtGa_2 , sealed in an evacuated (10^{-2} Torr) quartz ampoule, and annealed at 1100 °C for three hours. The samples were then homogenized at 875 °C for two months, after which time they were quenched in iced water.

These new samples turned from brass-colored to silver-colored during quenching. X-ray diffraction patterns of pulverized new sample corresponding primarily to the fluorite structure, along with many weaker peaks of another unidentified phase. After much experimentation, the intensities of the fluorite diffraction peaks relative to those of the unidentifiable peaks were determined to be functions of annealing temperature, quenching rate, and heat treatment subsequent to sample pulverization. In particular, it was determined that if the sample were annealed at low temperatures after pulverization, the intensities of the unidentifiable diffraction peaks became very great, whereas those peaks corresponding to the fluorite structure virtually disappeared. Additionally, if a pulverized sample were rapidly quenched from about 300 °C or higher, its diffraction pattern corresponded to that of the fluorite structure.

In the present investigation, chips of the old Baughman samples were heated to about 200 °C and cooled at various rates to nearly 77 K both under an optical microscope and in an X-ray diffraction precession instrument without any color change or change in diffraction pattern being observed. Additionally, powdered specimens of the old samples were annealed at 300 °C for three days, furnace-cooled to room temperature, and then analyzed by X-ray diffraction. No differences in X-ray diffraction patterns were observed between the annealed powders and freshly pulverized powders of the old samples.

Both the new sample and the old Baughman sample were compositionally analyzed using electron probe microanalysis, employing elemental Pt and a commercially produced GaAs wafer as standards for wavelength-dispersive spectroscopy. A significant difference in composition was found between the old brass-colored and new silver-colored samples. The new sample contained 33.1(2) at.% Pt, whereas the old sample comprised 34.3(1) at.% Pt, based on the average of five different measurements for each sample. Thus, while the new sample is very close in composition to the ideal stoichiometry of PtGa_2 , the old sample is substantially Ga-poor, corresponding more closely to the formula PtGa_{2-x} where $x \sim 0.085$.

Tiny fragments of the silver-colored samples were examined by precession photography, and those shown to be single rather than twinned crystals were examined further in order to characterize their crystal structure. On several such fragments, Mo K_α radiation intensity data sets (to 3330 reflections) were collected. These extensive data sets were used to determine whether any weak maxima might be present which violated the body centered lattice or the extinctions

expected for the space group $I4_1/acd$. Averaged cell dimensions from four smaller fragments are $a = 8.5544(4)$ and $c = 21.574(17)$ Å. Because of the high absorption cross section for Pt, as well as the irregular shapes of the X-ray specimens, empirical radiation absorption corrections were necessary. Data from the thinner, more needle-like fragments were eventually combined (579 symmetry-inequivalent hkl reflections) and employed in the final structural determination. The crystal structure was determined by Patterson and successive Fourier methods, coupled with least-squares refinements. Final atomic positional and displacement (thermal) parameters ($R = 0.0392$, $wR = 0.0434$) are given in Table 1. The final difference Fourier synthesis was carefully examined for any residual electron density peaks, particularly at interstitial sites which should be vacant, for any indication of the presence of impurity atoms.

Table 1. Atomic Position Coordinates and Displacement Parameters of Silver-Colored PtGa₂

Space Group: $I4_1/acd$ (No. 142)

Origin Choice 2 (Origin at $\bar{1}$ at 0, -1/4, 1/8 from $\bar{4}$)

Atom	Site	x/a	y/b	z/c	U _{eqv}
Pt1	16 d	0	1/4	0.01858(3)	100(3)
Pt2	16 f	0.19080(4)	x+ 1/4	1/8	64(2)
Ga1	32 g	0.27711(12)	0.20392(12)	0.06168(5)	98(5)
Ga2	32 g	-0.04891(12)	0.52520(12)	0.06053(6)	145(6)

U_{eqv} is calculated from the anisotropic displacement parameters using the definition $U_{eqv} = 1/3 \text{Tr} U$ and are in units 1000 Å². Numbers in parentheses following refined parameters represent one standard deviation in the last digit(s).

RESULTS AND DISCUSSION

The Crystal Structure of Silver-Colored PtGa₂

The structure of the silver-colored form of PtGa₂ may be described as alternating layers of Pt and Ga atoms stacked along the c axis of the tetragonal unit cell. Two crystallographically different Pt layers, Pt1 at $z \sim n/4$ and Pt2 at $z = (2n + 1)/8$, are interwoven by layers containing both Ga1 and Ga2 at $z \sim (2n + 1)/16$ (where $n = 0, 1, 2, \dots$). This complex structure may best be visualized by examining a basic unit consisting of the first four layers of atoms of the unit cell. The complete crystal structure may be obtained by applying symmetry operations to this unit of four layers, as will be discussed below. These layers are depicted on the right-hand side of Fig. 1, in a projection along the c -direction of the unit cell. Pt1 (large, white circles) form an essentially square, but slightly buckled array centered about $z = 0$. Pt1 containing a "+" sign are located at $z = 0.019$, whereas Pt1 containing a "-" sign are located at $z = -0.019$. Owing to this buckling, the arrangement of Pt1 may best be visualized as a face-centered square net in which the face-centered atoms are slightly displaced along c with respect to their four nearest neighbors. Pt2, depicted as large shaded circles, form an array of near squares and rhombi at $z = 1/8$, the squares being rotated about 10° relative to the a axes. Ga1 and Ga2 (small, black circles) are virtually coplanar, and form nets of near squares, near rectangles and trapezoids at $z \sim 1/16$ and $z \sim 3/16$. In the Ga net at $z \sim 3/16$, the positions of individual Ga1 and Ga2 are virtually transposed with respect to their positions in the net located at $z \sim 1/16$. On the scale of Fig. 1, the Ga nets at $z \sim 1/16$ and $z \sim 3/16$ are coincident in a projection along the c -direction; the two nets therefore appear to be

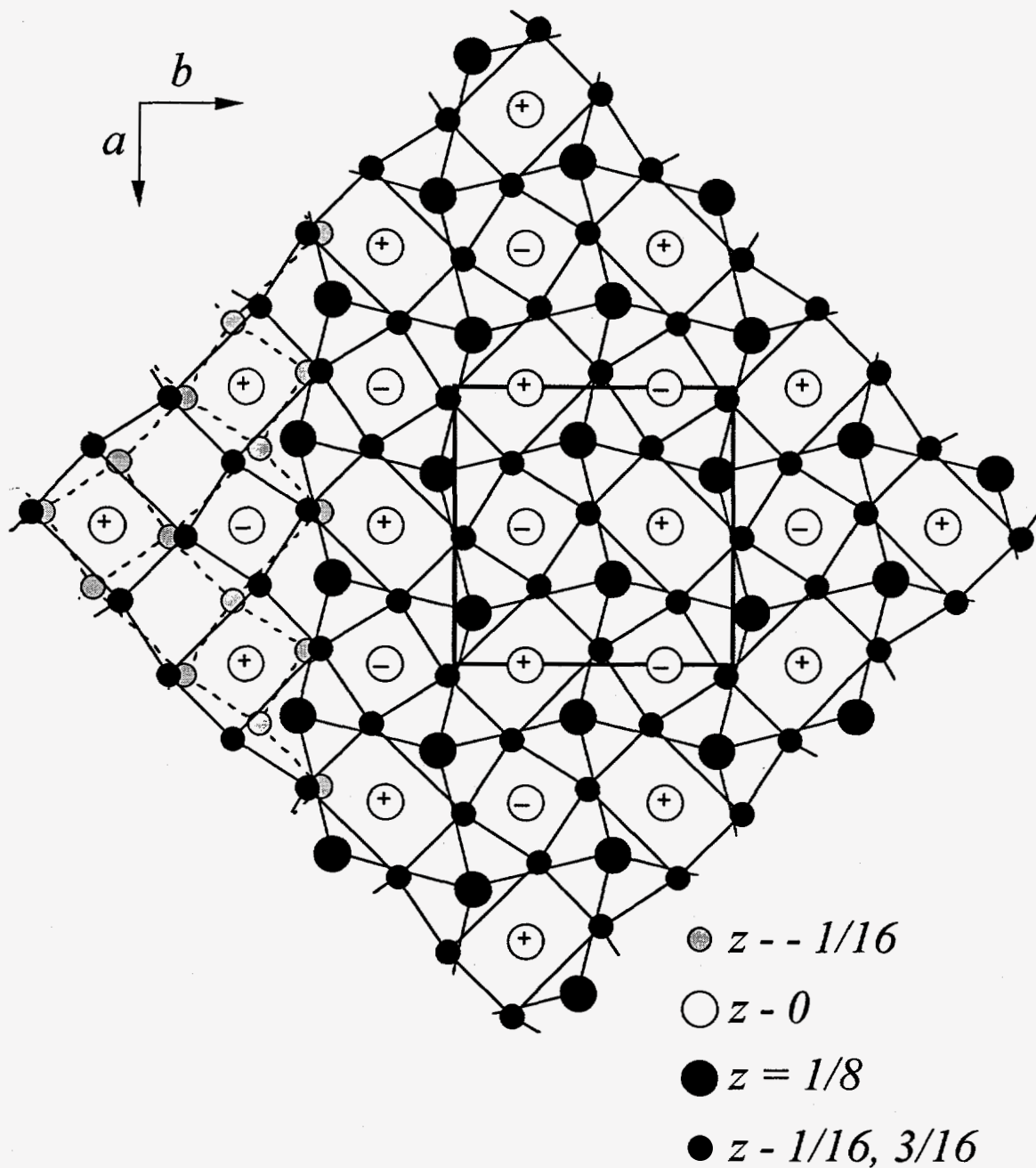


Fig. 1. A partial projection of the structure of silver-colored $PtGa_2$ as viewed along the c axis. The boundaries of the unit cell are denoted by the bold square near the center of the figure. Refer to the text for further details pertaining to the figure.

superimposed in the figure. However, in actuality the individual Ga possess slightly different x-y coordinates from one layer to the next.

In order to show the nearest neighbor environment of Pt1, a small portion of the Ga net at $z \sim -1/16$ (lightly shaded, small circles connected by dashed lines) has been included in the far left-hand region of Fig. 1. In addition, for the sake of clarity, the net of Pt2 has been removed from this region of the figure.

The full unit cell of silver-colored $PtGa_2$ consists of 16 layers of atoms: 4 of Pt1, 4 of Pt2 and 8 of Ga1 + Ga2. The remaining 12 layers of atoms may be generated either by 1.) translating the four atomic layers described above by $(1/2, 0, 1/4)$ and then applying the body-centering

translations ($1/2, 1/2, 1/2$) to each of these sets of layers, or 2.) successively applying the 4_1 symmetry operation about the screw axis at $(1/4, 0)$. (The entire unit cell may be produced making three transparent foils of Fig. 1 arranged atop the original figure according to these symmetry operations.)

The idealized near-neighbor environment about both Pt1 and Pt2 consist of eight Ga which form the corners of trapezoidal prisms. The edges of these prisms are shared by neighboring Pt. The trapezoidal prisms surrounding Pt1 may be seen in the far left-hand region of Fig. 1. Their tops and bases are perpendicular to the c axis, and are formed by the near squares and near rectangles, respectively, found within the Ga nets. The tops and bases are slightly twisted with respect to each other, with the remaining faces folded slightly along one of the diagonals. The trapezoidal prisms about Pt1 at $z = 0.019$ are upside-down (base facing up), whereas the prisms about Pt1 at $z = -0.019$ are rightside-up (top facing up). The trapezoidal prisms surrounding Pt2 lie on their sides (*i.e.*, with their tops and bases essentially perpendicular to the c direction), as may be seen in the right-hand side of Fig. 1. They comprise a larger, near rectangular, base and a smaller, near rectangular, top, which alternate about a vacant interstitial site at $(0, 1/4, 1/8)$, situated about $1/8c$ above a Pt1. Two sides of the prisms are formed by the trapezoids found within the Ga nets.

Both Ga have similar environments as well, consisting of four Pt and five Ga. The neighboring Ga form a distorted pentagonal pyramid, while the neighboring Pt form a very distorted tetrahedron (one angle of 78.7° opposite the tip of the pyramid; other angles grouped $114.7 + 2^\circ$).

The nearest neighbor Ga-Pt distances range from 2.55 to 2.65 Å, whereas the Ga-Ga distances range from 2.70 to 2.78 Å. The Ga-Pt contacts are, on average, slightly smaller for Pt1 than Pt2, while Ga1 has a slightly larger spread of both Pt and Ga contacts than does Ga2. Similar Pt-Ga (2.54 to 2.70 Å) and Ga-Ga (2.61 to 2.93 Å) distances have recently been observed in $\text{Ce}_2\text{Pt}_6\text{Ga}_{15}$ [6]. The longest Ga-Ga separations observed in this latter phase are influenced by the large Ce-Ga separations (3.13 to 3.37 Å) found in that structure. Although the Ga-Pt distances found in silver-colored PtGa_2 are close to those observed in its fluorite-structured modification (2.56 Å), the Ga-Ga distances are significantly shorter than those present in the cubic polymorph (2.96 Å).

The Phase Stability of PtGa_2

Our results suggest that the accepted Ga-Pt phase diagram [5] is incorrect in the compositional vicinity of PtGa_2 . First, rather than decomposing eutectoidally into Pt_3Ga_7 and Pt_2Ga_3 , PtGa_2 undergoes a transformation near 150°C from the brass-colored fluorite structure to the silver-colored tetragonal structure. The experimental data of previous researchers may have been misinterpreted in this regard (*i.e.*, the complicated diffraction pattern of tetragonal PtGa_2 , decomposed microstructure of PtGa_2 and the thermal arrests at 153°C are due to a polymorphic transformation rather than eutectoidal decomposition [2]).

Second, the compositional analysis of the sample grown by Baughman indicates that fluorite-structured PtGa_2 exists over a range of homogeneity and is not a line compound as depicted in the assessed Ga-Pt phase diagram. Its chemical formula is more appropriately expressed as PtGa_{2-x} , where at the very least $0 < x < 0.085$. However, because Baughman's boules were grown at high temperatures and subsequently quenched, it is unclear whether fluorite-structured PtGa_2 exhibits a range of homogeneity at low temperatures under equilibrium conditions.

Why are Ga-poor samples resistant to transformation while stoichiometric samples transform readily? We believe that the effect is due to kinetic limitations induced by the low temperature of the structural transformation. If the silver-colored tetragonal form of PtGa_2 were a line compound, then Pt_2Ga_3 would have to precipitate from Ga-poor, fluorite-structured PtGa_2 before it could transform to the tetragonal polymorph. However, such precipitation would necessarily entail long-range diffusion, a process that would be exceedingly slow at 153°C , the assumed equilibrium temperature of transformation. If precipitation of Pt_2Ga_3 were precluded, it is plausible that nonstoichiometric PtGa_2 could remain indefinitely in the fluorite-structured modification.

A striking parallel may exist between PtGa_2 and ZrO_2 . ZrO_2 possesses the fluorite structure at high temperatures, transforming to a tetragonal and then monoclinic modification upon cooling. It is not possible to retain ZrO_2 in its fluorite-structured modification at room temperature. However, doping ZrO_2 with an aliovalent cation, such as Ca^{2+} or Y^{3+} , leads to the development of anion vacancies and a cation-rich phase. Such defect- or impurity-stabilized ZrO_2 may easily be retained at room temperature by quenching.

CONCLUDING REMARKS

Recently the crystal structure of $\text{Ga}_8\text{Ir}_4\text{B}$ was determined [7]. $\text{Ga}_8\text{Ir}_4\text{B}$ is essentially isostructural with silver-colored PtGa_2 , except that in $\text{Ga}_8\text{Ir}_4\text{B}$, the B atoms occupy an atomic site (0, 1/4, 1/8) which is vacant in PtGa_2 . The existence of an isostructural, ternary boride raises the question of whether the silver-colored form of PtGa_2 might be stabilized by impurities, such as O or C, on these or similar vacant atomic sites. The Fourier maps generated in the present investigation were carefully examined without discovering any electron densities on such atomic sites. Specifically with respect to the (0, 1/4, 1/8) sites, the electron density is zero.

The high-temperature fluorite to the low-temperature tetragonal transformation of PtGa_2 appears to be driven by the substantial decrease in atomic volume afforded by such a change. If the atomic volumes of the intermediate phases in the Ga-Pt system are plotted as a function of composition, one notes that the atomic volume of fluorite-structured PtGa_2 is anomalously large relative to the atomic volumes of the remaining phases from elemental Ga to elemental Pt; however, tetragonal PtGa_2 lies in its anticipated position. Therefore, upon transforming from the cubic to the tetragonal structure, PtGa_2 achieves an atomic volume that is consistent with those of the other platinum gallides.

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