The Hexagonal Laves Phase MgIr₂

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The hexagonal Laves phase MgIr₂ was synthesized from the elements in a sealed tantalum tube in an induction furnace. MgIr₂ was investigated by powder and single crystal X-ray data: \( P_6_3/m n m \), \( a = 516.9(1) \) pm, \( c = 838.5(2) \) pm, \( wR_2 = 0.0771 \), \( 135 \) \( F^2 \) values, and 11 variable parameters. The magnesium atoms have coordination number (CN) 16 (12 Ir + 4 Mg), while the smaller iridium atoms, Ir₁ and Ir₂, both have CN 12 (6 Ir + 6 Mg). The Ir–Ir distances within the three-dimensional network of face- and corner-sharing Ir₄/2 tetrahedra range from 250 to 267 pm. The magnesium atoms have one shorter (306 pm) and three longer (319 pm) magnesium contacts. The crystal chemistry of MgIr₂ is briefly discussed and compared with the other binary Mg-Ir intermetallics.

Key words: Magnesium, Iridium, Crystal Structure, Solid State Synthesis

Introduction

The binary system magnesium–iridium is characterized by the intermetallic compounds \( \text{Mg}_2\text{Ir}_4 \) (12.1 at.-% Ir) [1], \( \text{Mg}_{44}\text{Ir}_7 \) (13.7 at.-% Ir) [2, 3], \( \text{Mg}_{33}\text{Ir}_3 \) (18.8 at.-% Ir, formerly reported with the approximate composition \( \text{Mg}_4\text{Ir}_4 \) [4, 5], \( \text{Mg}_2\text{Ir} \) (25 at.-% Ir) [6], \( \text{Mg}_4\text{Ir}_2 \) (28.6 at.-% Ir) [7], \( \text{MgIr} \) (50 at.-% Ir) [8], and \( \text{Mg}_8\text{Ir}_2 \) (54 at.-% Ir) [9]. Our recent phase analytical investigations in the iridium rich part of the phase diagram revealed the hexagonal Laves phase MgIr₂ as the so far most iridium rich compound. The synthesis and structure refinement of MgIr₂ are reported herein.

Experimental Section

Synthesis

Starting materials for the preparation of the MgIr₂ samples were a magnesium rod (Johnson Matthey, \( \odot \) 16 mm, > 99.5%) and iridium powder (Degussa-Hüls, 200 mesh, > 99.9%). Pieces of the magnesium rod (the surface of the rod was first cut on a turning lathe in order to remove surface impurities) and a cold-pressed pellet of iridium (\( \odot \) 6 mm) were weighed in the atomic ratio \( 2\text{Mg}:3\text{Ir} \) and put in a glassy carbon crucible (SIGRADUR®G, type GAZ006). The latter was placed in a water-cooled sample chamber [10] of an induction furnace (Hüttinger Elektronik, Freiburg, Typ TIG 1.5/300). The mixture of the elements was first heated under flowing argon up to \( ca. \) 1300 K. The argon was purified over silica gel, molecular sieves, and titanium sponge (900 K). After the melting procedure the sample was cooled within 30 min to \( ca. \) 1200 K and held at that temperature for another 30 min. Then the sample was cooled within one hour to \( ca. \) 700 K and finally quenched by switching off the furnace. The light gray sample could easily be separated from the glassy carbon crucible. No reactions whatsoever with the crucible material could be detected.

The X-ray powder patterns of this sample showed MgIr [8] and iridium as reaction products. The inductively melted ingot was then ground to powder in a steel mortar, cold-pressed to a pellet of 6 mm diameter and placed in a tantalum tube. This tube was first heated to \( ca. \) 1400 K, cooled...
to ca. 1300 K within 30 min, kept at that temperature for another 30 min, cooled to 700 K within one hour and finally quenched to room temperature. The sample is stable in air as a compact button as well as a fine-grained powder. Single crystals exhibit metallic luster.

The MgIr2 single crystal investigated on the imaging plate diffractometer and the bulk sample have been analyzed by an EDX measurement using a LEICA 420 I scanning electron microscope with MgO and iridium as standards. No impurity elements were detected. The analyses $33 \pm 2$ at.-% Mg : $67 \pm 2$ at.-% Ir are in excellent agreement with the ideal composition of $33.3$ at.-% Mg : $66.7$ at.-% Ir.

**X-ray film data and structure refinement**

The MgIr2 sample was characterized through its Guinier powder pattern using Cu-Kα1 radiation and α-quartz ($a = 491.30$, $c = 540.46$ pm) as an internal standard. The Guinier camera was equipped with an image plate system (Fujifilm BAS–1800). The indexing of the powder data was facilitated by an intensity calculation [11] using the atomic parameters of the refined structure. The hexagonal lattice parameters (Table 1) were obtained by least-squares fits of the Guinier data.

Irregularly-shaped single crystals were isolated from the annealed sample by mechanical fragmentation and examined on a Buerger precession camera (equipped with an imaging plate system Fujifilm BAS–1800) in order to establish suitability for intensity data collection. Single crystal intensity data were collected at room temperature on a Stoe IPDS–II diffractometer with graphite monochromatized Mo-Kα radiation. All relevant crystallographic data for the data collection and evaluation are listed in Table 1.

The isotypism of MgIr2 with the hexagonal Laves phase MgZn2 [12] was already evident from the X-ray powder data. The atomic positions of the prototype MgZn2 [12] were taken as starting values and the structure was refined using SHELXL-97 [13] with anisotropic atomic displacement parameters for all sites. As a check for the correct composition, the occupancy parameters were refined in a separate series of least-squares cycles. The occupancy parameters varied between $99(1)$% for Ir2 and $103(7)$% for Mg. Thus, all sites were fully occupied within one standard deviation. In the last cycles, the ideal occupancies were assumed again. A final difference Fourier synthesis revealed no significant residual peaks (see Table 1). The highest residual peaks were all close to the iridium sites (137 pm to Ir2) and most likely resulted from an incomplete absorption correction of this highly absorbing compound. The positional parameters and interatomic distances are listed in Tables 2 and 3. Further details on the structure refinement are available.*

**Discussion**

MgIr2 crystallizes with the structure of the hexagonal Laves phase MgZn2 [12] (Fig. 1). As emphasized in the Figure, the Ir1 and Ir2 atoms build up rows of face- and corner-sharing Ir$_{4/2}$ tetrahedra along the $c$ axis. These are connected via Ir–Ir bonds within the $ab$ planes at $z = 1/4$ and $z = 3/4$ forming a three-

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*Details may be obtained from: Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), by quoting the Registry No. CSD-414084.
dimensional network. The Ir–Ir distances within the tetrahedral network range from 250 to 267 pm. These Ir–Ir distances are all shorter than in \textit{fcc} iridium [14] where each iridium atom has twelve iridium neighbors at 272 pm. Even shorter Ir–Ir distances occur in the complex structures of Mg$_{2.3}$Ir$_{0.7}$ [9] (245 and 258 pm) and MgIr [8] (245–266 pm). Thus, Ir–Ir bonding plays certainly an important role in this Laves phase. The Mg–Ir distances (300–304 pm), on the other hand, are significantly longer than the sum of the covalent radii of 262 pm for iridium and magnesium [15]. Each magnesium atom in MgIr$_2$ has four nearest magnesium neighbors at Mg–Mg distances of 306 and 319 pm. These compare well with the average Mg–Mg distance of 320 pm in \textit{hcp} magnesium [14].

The coordination polyhedra of the MgIr$_2$ structure are shown in Fig. 2. The magnesium atoms have (CN) 16 (12 Ir + 4 Mg), while the smaller iridium atoms, Ir1 and Ir2, both have CN 12 (6 Ir + 6 Mg). The 12 neighbors around the Ir1 and Ir2 sites have slightly distorted icosahedral arrangements. The three different coordination polyhedra in the MgIr$_2$ structure are slightly distorted Frank-Kasper polyhedra [16, 17]. At this point it is interesting to note, that the structure of Mg$_{2.3}$Ir$_{0.7}$ [9], with a slightly smaller iridium content, contains slabs of the MgIr$_2$ structure.

Laves phases can adopt three different structures, \textit{i.e.} the cubic MgCu$_2$ or the hexagonal MgZn$_2$ and MgNi$_2$ types [18–21, and ref. therein]. Which type occurs depends on electronic as well as on geometrical features. Johnston and Hoffmann [20] have investigated the structure–bonding relationships in Laves phases by performing extended Hückel band structure calculations. These studies revealed that the type of the Laves phase depends on the valence electron concentration (VEC). The AIr$_2$ Laves phases with $A=$ alkaline earth and rare earth metals, Zr, Th, U, and Np [22–24] crystallize all with the cubic MgCu$_2$ type structure. The cubic AIr$_2$ compounds with a divalent $A$ component have all 20 valence electrons per formula unit. According to the diagrams of Johnston and Hoffmann [20], the compounds with VEC = 20 are at the border between the hexagonal and the cubic network. For MgIr$_2$ described herein, the much smaller size of magnesium seems to favor the hexagonal MgZn$_2$ type.

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