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Crystal growth of the high-pressure phase of Mg_2Sn

T.I. Dyuzheva, N.A. Bendeliani, L.N. Dzhavadov, T.N. Kolobyanina, N.A. Nikolaev

The Institute of High Pressure Physics of the Russian Academy of Sciences, 142092, Troitsk, Moscow Region, Russia

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Abstract

Phase relations in the Mg_2Sn–Sn system were studied by differential thermal analysis at a pressure of 5.8 GPa and temperatures up to 1100 °C. A schematic p, T diagram for Mg_2Sn is presented. Single crystals of the high-pressure phase of Mg_2Sn were obtained by growth from a molten solution under high pressure. Crystal data for Mg_2Sn II were determined using a Buerger precession X-ray camera. The phase Mg_2Sn II crystallizes with hexagonal unit cell, $a = 13.19 \pm 0.01$ Å, $c = 13.28 \pm 0.01$ Å, $c/a = 1.006$, $D_m = 4.1 \pm 0.2$ g cm^{-3}, $z = 30$, $D_c = 4.17$ g cm^{-3}, space group $P3c1$ (no. 158) or $P\bar{3}c1$ (no. 163).

Keywords: Crystal growth; High-pressure phase; Phase relations; Differential thermal analysis

1. Introduction

Mg_2Sn belongs to a large group of intermetallic compounds AX_2, where A≡Mg or an alkaline earth and where X is one of the elements Si, Ge, Sn or Pb. Under normal conditions the Mg_2X compounds are narrow band gap semiconductors and crystallize in the fluorite-type structure type (CaF_2). The substitution of a large-size alkaline earth for Mg results in a change in structure type from fluorite to cotunnite (α-$PbCl_2$). There have been several attempts to transform Mg_2X compounds from the fluorite to the cotunnite structure under high pressure. New dense phases were obtained for Mg_2Si, Mg_2Ge and Mg_2Sn, which are metastable under normal conditions. However, the structures of the high-pressure phases are strong distortions of the cotunnite type [1–4]. Since a similar distortion is associated with the semiconductor–metal transition, it is of interest to solve the structure of the high-pressure phases. The present study was undertaken to grow single crystals and to determine the symmetry of the high-pressure phase of Mg_2Sn.

2. Experimental procedure

Starting samples of the required composition were prepared by pressurizing mixtures of the corresponding pure elements, involving a treatment at high pressure and temperature. X-ray powder diffraction analysis of the final products was carried out using a standard Debye–Sherer camera with filtered copper radiation.

A pressure chamber of the profiled anvil type was used. The pressure was determined and controlled by a preliminary calibration based on the phase transitions in Bi and PbTe at room temperature and on the melting points of Cu and Mg at high temperature. The error in determination of the pressure was ±2%. Fig. 1 shows the reaction cell. The graphite heater was placed in a pressurized NaCl collar. The geometry of the heater prevents noticeable temperature gradients internally and allows the sample and the thermocouple to be located in a more convenient manner. The sample container, which is also made of pressed NaCl powder, takes care of sealing and chemical inertia for the sample over the duration of the experiment. For differential thermal analysis (DTA) measurements the thermocouple, in ceramic cladding, was introduced between two pellets of a sample, pressed beforehand and placed in the hermetically sealed NaCl container. The total weight of a sample was 200 mg. Fig. 1 shows the reference thermocouple only. The temperature was measured with a chromel–alumel thermocouple, neglecting pressure correction.

Program-controlled temperatures were used for a given operating condition, deviation of the temperature did not exceed ±0.5 °C. Apparently, the actual temperature fluctuation of the sample is even smaller than 0.5 °C because of the heat resistance between the heater and the thermocouple is smaller than that between the heater and the sample (the thermal diffusivity of the

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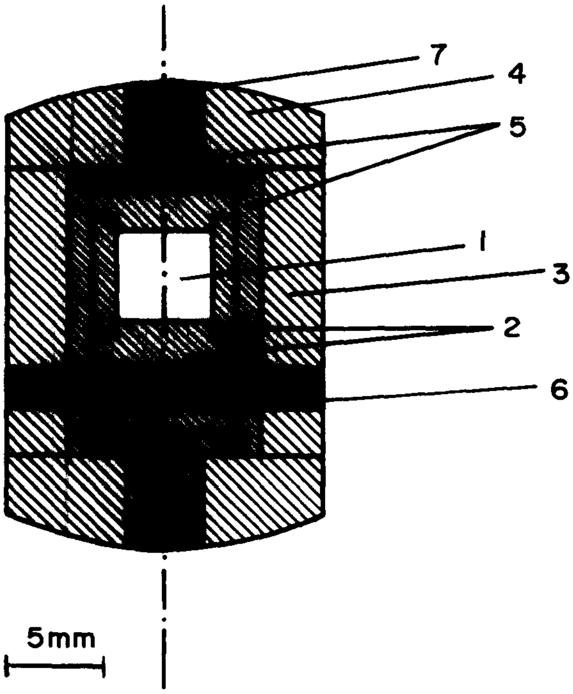

Fig. 1. The reaction cell for crystal growth and DTA measurements: 1 sample, 2 pressed NaCl powder container, 3 pressed NaCl powder collar, 4 pressed NaCl powder cap, 5 graphite heater, 6 thermocouple in ceramic cladding, 7 Ta tips.

thermocouple material is large in comparison with the thermal diffusivity of NaCl, containing the sample).

3. Results and discussion

The high-pressure phase of Mg_2Sn is formed at $p>3$ GPa and $T>600$ °C and remains metastable under normal conditions. As the position of the triple point (Mg_2Sn I–Mg_2Sn II–liquid) in the p,T diagram is unknown, all crystal growth experiments were performed at $p=5.8$ GPa to remain in the stability region of Mg_2Sn II.

The solubility of Sn in the initial Mg_2Sn I phase is close to zero under normal conditions [5]. One could assume that the high-pressure Mg_2Sn II modification would also preserve its stoichiometry in the presence of Sn. It would then be possible to grow single crystals of the high-pressure phase more simply, i.e. from a molten solution. Indeed, powder diffraction patterns of the Mg_2Sn II samples with excess Sn were identical with patterns of the stoichiometric samples. Using DTA measurements, phase relations in the Mg_2Sn–Sn system were obtained. Fig. 2 presents the T,x diagram at 5.8 GPa within the Mg_2Sn–Sn composition interval. The schematic p,T diagram of Mg_2Sn shown in Fig. 3 was constructed from the enthalpy of fusion at normal pressure [6], the pressure transition Mg_2Sn I–Mg_2Sn II in situ [2], and the melting data of the high-pressure

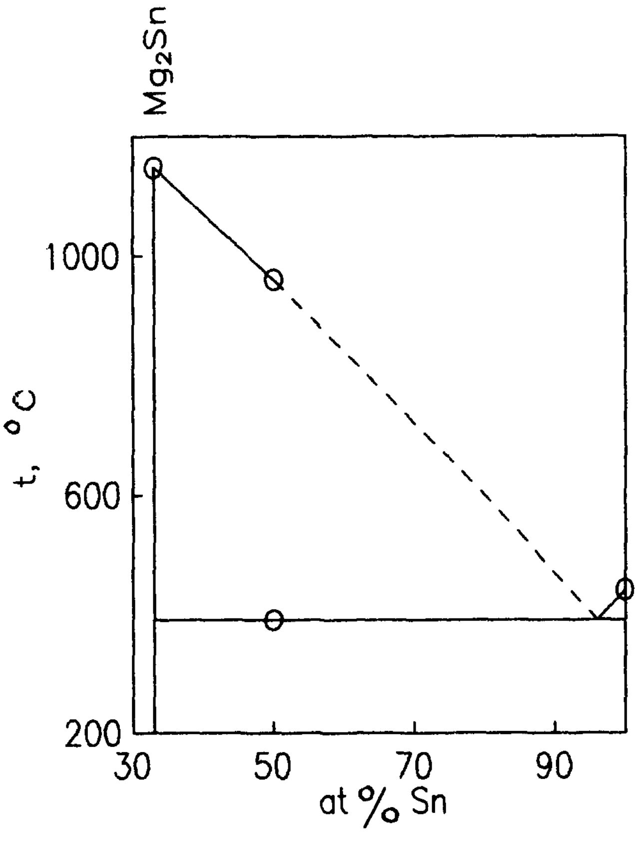

Fig. 2. T,x diagram of the Mg_2Sn–Sn system at $p=5.8$ GPa.

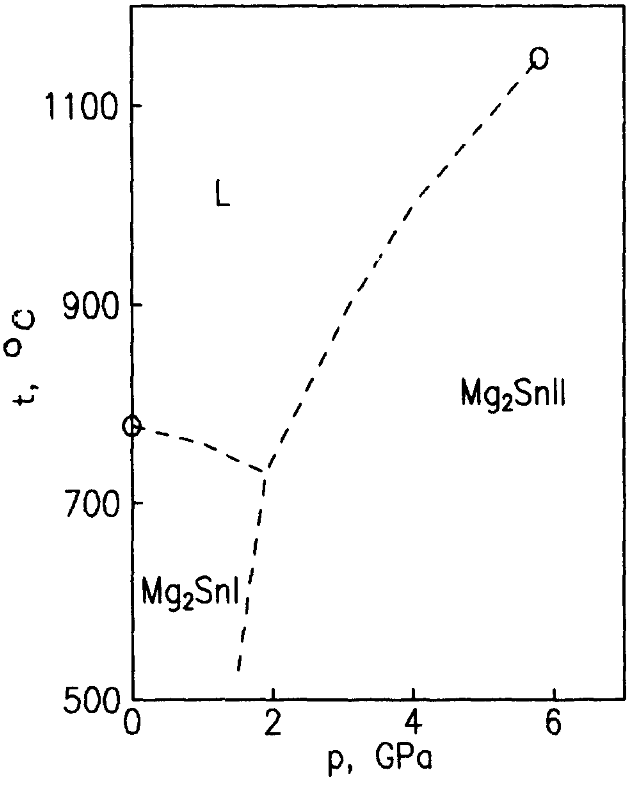

Fig. 3. Schematic p,T diagram for Mg_2Sn.

phase (present work). It follows from Fig. 2 and Fig. 3 that the high-pressure phase Mg_2Sn II is stable up to the melting point at 5.8 GPa and melts congruently. The eutectic type of phase diagram, which is characteristic for normal conditions, is retained under high pressure.

An essential difference in the melting points of Mg_2Sn II and Sn provides a stability region favourable for crystal growth from the molten solution. In accordance with the available data, the sample composition 50at.%Mg–50at.%Sn and the appropriate temperature regime were chosen. The growth procedure was carried out as follows: compression to the given pressure; heating up to 900 °C for 20 min; heating up to 1020 °C for 10 min; holding at 1020 °C for 30 min; cooling down to 320 °C at a rate of 1 °C min^{-1} for 8 h; cooling down to room temperature for 10 min; unloading. The temperature decrease of 700 °C resulted in a pressure decrease of 0.6–0.8 GPa during the growth process because of thermal compression of the reaction cell, and resulted in a temperature decrease of the eutectic and the liquidus by 30–50 °C. The velocity of crystallization also decreased slightly. However, as long as the sample remained in the stability region of Mg_2Sn II, the load remained constant.

The final products were a compact eutectic mixture with single-crystal inclusions of Mg_2Sn II. The crystal sizes were about 1 mm. The crystals were extracted by breaking the sample since other methods were unsuccessful. Some monocrystal fragments with dimensions 0.1–0.2 mm were selected for an X-ray diffraction study. Precession photographs were taken from preliminary examination of the fragments and the space group. The Laue group was found to be $\bar{3}m$. The zeroth to third layers around the a axis and zeroth to third layers around the c axis were recorded with Mo Kα radiation. The unit cell was found to be hexagonal with $a = 13.19 \pm 0.01$ Å, $c = 13.28 \pm 0.01$ Å. The systematic extinctions ($h\bar{h}0l$, $l = 2n$) indicated the space group to be $P\bar{3}c1$ or $P3c1$. Consideration of crystal chemistry appears to favour $P\bar{3}c1$ since there are 30 molecules in the unit cell, based on a measured density of 4.1 ± 0.2 g cm^{-3}, which correlates with the computed density 4.17 g cm^{-3}. Structure determination is now in progress.

Acknowledgment

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