SOVIET PHYSICS – CRYSTALLOGRAPHY VOL. 17, NO. 4 JAN.-FEB., 1973

L. Merrill

POLYMORPHISM OF Mg_2Sn AT HIGH TEMPERATURES AND PRESSURES

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Translated from Kristallografiya, Vol. 17, No. 4,
pp. 804-811, July-August, 1972
Original article submitted July 13, 1971

An x-ray investigation of the effect of high pressures and temperatures on the structure of the compound Mg_2Sn was carried out. Under normal conditions it has the antifluorite structure, which at 25°C with p ~ 30 kbar undergoes a reversible first-order phase transition, while at ~40 kbar and 400°C it undergoes an irreversible polymorphic transition with the formation of a metastable phase. It is shown that the structures of the high pressure phases obtained during the reversible and irreversible transitions are identical. The density is determined (pycnometrically) for the metastable phase Mg_2SnII ($\rho_e = 4.1 \pm 0.2$ g/cm^3) and the parameters of the hexagonal unit cell are $a_0 = 13.18 \pm 0.02$ Å and $c_0 = 6.99 \pm 0.04$ Å with z = 15. A new hexagonal structure model is proposed for the high-pressure phase of Mg_2SnII with a motif similar to Ni_2Si.

The effect of high pressures on the crystal structure of Mg_2Sn for pressures up to 100 kbar and temperatures from room temperature to 400°C has been studied using x rays. Under ordinary conditions Mg_2Sn crystallizes in the antifluorite structure type with parameters $a_0 = 6.7630$ Å and $\rho_p = 3.592$ g/cm^3 [1]. According to the data obtained at p ~ 30 kbar and t = 25°C a reversible polymorphic transition is established which has previously been observed from measurements of the electrical resistance and the Moller isomer shift and also using x rays by Drickamer and Christoe [2]. The diffraction pattern which we have found clearly does not correspond to the suggestion set forth in [2] of cubic symmetry of the high-pressure phase, which was taken to be bcc or primitive cubic. It should be noted that the experimental diffraction data was not given in [2].

In the present work our high-pressure x-ray camera could be used at room temperature [3] and elevated temperatures [4]. To estimate the pressure in some cases NaCl powder was added to the material investigated, as a standard; the pressure was determined using the semiempirical equation of state for NaCl given by Decker [5].

Table 1 presents x-ray data for high-pressure phases with p = 70 ± 3 kbar at 25°C obtained in filtered Mo radiation.

X-ray patterns of Mg_2Sn taken at 40 kbar and 400°C in filtered Mo radiation turn out to be identical to x-ray patterns obtained at this pressure at room temperature. However, upon removing the pressure in this case the high-pressure phase is preserved indefinitely in the metastable state at 25°C. The results of a comparison of the diffraction data are given in Table 2. The metastable nature of the high-pressure phase Mg_2SnII at 25°C is demonstrated by annealing for 1 h at 300°C, resulting in complete transformation of Mg_2SnII into Mg_2SnI (the antifluorite structure).

Thus it turns out that the modification Mg_2SnII can be retained in the metastable state at normal conditions only if it is produced at high temperature. Such behavior can be explained if we assume that at high temperatures the nuclei of the low-pressure phase Mg_2SnI anneal out in the stable region of the phase Mg_2SnII. Moreover, Mg_2Sn always contains a small amount of β-Sn as an impurity which evidently can also facilitate retention of Mg_2SnII in the metastable state. Some analogy