

High Pressure Phase of MgTe: Stable Structure at STP?

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The crystal structure of MgTe has been studied in a diamond anvil cell using energy dispersive x-ray diffraction to 60 GPa at room temperature. The first pressure-induced structural phase transformation among magnesium chalcogenides was observed for MgTe at $P \approx 1-3.5$ GPa. The new phase has been indexed as the NiAs structure and it persisted after unloading to low pressure (0.2 GPa) and annealing for 10 h at 100 °C. This is the first experimental evidence consistent with a recent theoretical prediction that for low temperature the ground state of MgTe is the NiAs structure. It is also the first pressure-induced wurtzite to NiAs transition.

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The II-VI compound wide-gap semiconductor MgTe is of both technological and scientific interest. MgTe is the end point of $\text{Mg}_x\text{Cd}_{1-x}\text{Te}$, $\text{Mg}_x\text{Mn}_{1-x}\text{Te}$, and $\text{Mg}_x\text{Zn}_{1-x}\text{Te}$ ternary systems all of which are promising optoelectronic materials [1-3]. The structural studies on MgTe are less than adequate mainly because of its high hygroscopicity [4]. Pioneer works by Zachariassen [5] and Klemm and Wahl [6] showed that MgTe has the hexagonal wurtzite structure. This result has been widely accepted and experimentally repeated [4,7]. However, recently Yeh *et al.* [8] did first-principles local-density formalism (LDF) calculations on MgTe and predicted the ground state of MgTe to be the NiAs structure at $T = 0$. In a separate theoretical study by Van Camp and Van Doren [9] the same conclusion has been reached despite some variations in the calculation scheme.

Understanding the sequence of high-pressure structures for magnesium chalcogenides is also of interest as a part of the larger goal of understanding the sequence for the $A^N B^{N-8}$ compounds in general. The combination of modern diamond anvil cell techniques and the use of synchrotron sources for x-ray diffraction have provided excellent opportunities for high quality crystalline structural studies up to multimegabar pressure. Within the larger picture of the alkaline earth chalcogenides, magnesium chalcogenides are of particular interest since no first-order structural phase transformation has been experimentally discovered so far. MgO is calculated to be stable in the NaCl(*B1*) structure to 600 GPa [10], and its equation of state has been determined up to 227 GPa [11]. In comparison CaO is known to have the $B1 \rightarrow B2(\text{CsCl})$ transition at 61 GPa [12], while CaTe transforms at 25 GPa to an intermediate phase and at 33 GPa to the *B2* structure [13]. Thus it is beneficial to start with MgTe to examine if the anomalously high transition pressure associated with MgO is a general trend of all magnesium chalcogenides.

This paper presents the experimental results of high-pressure energy-dispersive x-ray diffraction experiments

we have performed on MgTe and the data analysis which leads to high-pressure crystal structure and equation of state determinations. This study is part of our global investigation on the structural and electronic properties of III-V and II-VI compounds under high pressure [13-16].

MgTe was prepared from the reaction of 34 mg magnesium nitride powder with 128 mg tellurium (Aldrich 99.9%) in a 20 cm³ sealed, evacuated quartz tube at 900 °C for 25 h. Care was taken to avoid an explosion by using a large enough tube for the nitrogen produced. The Mg_3N_2 was prepared by flowing anhydrous ammonia (Matheson Gas Corp.) over magnesium raspings (Strem Chemicals 99.9%) at 750 °C for 16 h. X-ray powder diffraction of the Mg_3N_2 showed it to be a single phase. Likewise after MgTe was made, only a single phase was present. The MgTe lattice parameters were redefined with LATCON-Z [17] to a hexagonal cell with $a = 4.550(1)$ Å and $c = 7.394(1)$ Å at 1 bar and room temperature, in agreement with the literature value of $a = 4.54$ Å and $c = 7.39$ Å [6]. All manipulations were performed in an argon-filled glove box. Five batches of MgTe powder have been made for this study by following the same procedure as described above.

For the first three experiments, the pressure vessel consisted of a diamond anvil cell (DAC) of the controlled displacement type [18], with diamond anvils of 600 μm flats. The sample chamber was a 200 μm diameter hole in a spring steel gasket preindented to 70 μm. For the last two experiments, diamond anvils of 300 μm flats were used with a 100 μm diameter sample chamber in a tungsten-rhenium gasket, which had been preindented to 50 μm. Except for the last experiment, in which a few small ruby chips were used, gold powder was loaded in the sample chamber as an internal pressure marker. Care was taken to ensure that the MgTe sample had no exposure to moisture: No pressure medium was used; sample grinding, DAC sample loading, and closing of the DAC were all performed in a dry argon environment.

Energy-dispersive x-ray diffraction (EDXD) experiments on MgTe were performed at the Cornell High Energy Synchrotron Source (CHESS). The diffraction geometry was calibrated with an unpressurized gold foil. Various diffraction angles 2θ of from 12.0° to 15.0° were used. The typical collection time for each spectrum was approximately 15 min; a longer time was spent once in every series of spectra to achieve higher quality. The pressure for each spectrum (except for those from the last experiment) was determined from the isothermal equation of state (EOS) of gold by Jamieson, Fritz, and Manghni [19] from the measured gold cell volume. For the last experiment the pressure is measured based on the (nonhydrostatic) ruby sale [20]. Ruby fluorescence measurements were performed on a Spex model 1877C triple monochromator with a cooled optical multichannel detector. The fluorescence signals were excited with the 488 nm line from an Ar^+ laser. The sample cell volume was also obtained from each EDXD spectrum. The pressure was then increased by decreasing the anvil separation and thus the measured EOS was generated. Further details of the experimental techniques and apparatus can be found elsewhere [18,21].

On uploading from 0 to 0.9 GPa all spectra indexed well to the wurtzite phase. The lattice constants at ambient conditions measured in the diamond cell by EDXD study are $a = 4.548 \text{ \AA}$, $c = 7.390 \text{ \AA}$. They are consistent with the literature values if we take into account the accuracy of $\Delta d_m/d_m = 2.5 \times 10^{-3}$ in EDXD interplanar spacing measurements [22]. Figure 1(a) shows a typical EDXD spectrum of MgTe in the wurtzite structure at 0.3 GPa. Table I shows the observed and calculated d spacings and integrated intensities. The agreement of the d spacings is excellent, but the integrated intensities have only fair agreement. This is typical for EDXD experiments using diamond anvil cells in which the sample is

TABLE I. List of the observed and calculated interplanar spacings (d) and intensities (I) of the wurtzite structure at 0.3 GPa. The calculation of relative intensities is discussed in Ref. [18].

(hkl)	d_{obs} (Å)	d_{calc} (Å)	I_{obs} (%)	I_{calc} (%)
(100)	3.935	3.935	11	7
(002)	3.690	3.696	8	9
(101)	3.475	3.474	30	33
(102)	2.692	2.694	18	20
(110)	2.272	2.272	100	100
(103)	2.089	2.088	55	60
(200)	1.968	1.968	8	10
(112)	1.935	1.936	32	53
(201)	1.902	1.902	47	28
(004)	N.A.	1.848	^a	5
(202)	1.739	1.737	3	10
(104)	1.668	1.673	3	5
(203)	1.537	1.538	2	25
(210)	1.486	1.488	2	8
(211)	1.457	1.458	7	23
(114)	1.435	1.434	5	12
(105) ^b	1.382	1.384	4	16
(204)	1.347	1.347	<1	2.3
(300)	1.312	1.312	2	9
(213)	1.272	1.273	3	22

^aThe MgTe (004) line is unresolvable from the Te $K\alpha$ lines.

^bThe (105) peak is indeed a mixture of (105) and (202); the relatively weak (202) is omitted for simplification.

also the pressure medium so that deformation under loading often exacerbated preferred orientation to give a less than ideal diffraction pattern. This could be compared to a case where a quasihydrostatic pressure was obtained by the use of a pressure medium (see Table I of Ref. [18]).

For spectra with pressures ≥ 3.5 GPa there was a dramatic change in the pattern of the sample diffraction lines, indicating a phase transformation. In order to determine the structure of the new phase the following two assumptions are made: (1) ~ 17 volume change (decrease) from the original to the new phase, and (2) the new structure has sixfold coordination versus the fourfold coordination of the original structure. Both of these assumptions have been found to be generally true for the high-pressure behavior of III-V and II-VI compounds.

The atomic volume V_a of the new phase after transition is estimated from the last spectrum of the original phase and the assumed volume collapse. Simulations of diffraction patterns from a series of candidate structures, including rocksalt, β -Sn, NiAs, anti-NiAs, WC, and cinnabar, were inspected by constructing the cell volume from V_a and adjusting possible internal variables over a reasonable range. The CsCl structure, although of eightfold coordination, was also examined. When we set $c/a = 1.63$ for NiAs, the simulation pattern showed striking agreement with the sample diffraction patterns, while other structures were readily rejected.

Under further examination, all our sample spectra in the new phase fit well to the NiAs(B8) structure; for

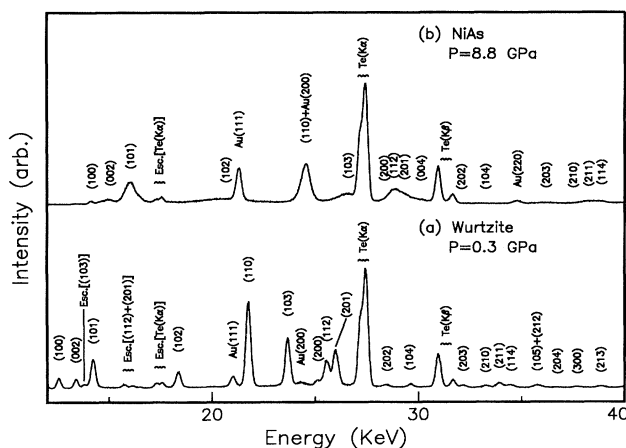


FIG. 1. EDXD diffraction spectra of MgTe. Au is gold; Esc. stands for the Ge detector escape peak(s) corresponding to the peak(s) in the bracket; all other labeled peaks are the sample. (a) Original wurtzite structure at 0.3 GPa. (b) The new high pressure NiAs structure at 8.8 GPa.

$P < 12$ GPa, a nearly constant c/a ratio of 1.633(6) was obtained. Figure 1(b) shows a typical EDXD spectrum of MgTe in the $B8$ structure at 8.8 GPa with $a = 4.029$ Å and $c = 6.563$ Å. Table II shows the observed and calculated d spacings and integrated intensities for the peaks observed below 40 KeV. The agreement of the d spacings is excellent, and the agreement of the integrated intensities is equivalent to that of the original phase before the phase transition.

The volume versus pressure data of the $B8$ phase was fit to the first-order Birch EOS (see Fig. 2):

$$P = \frac{3}{2}B_0(x^{7/3} - x^{5/3})\left[1 + \frac{3}{4}(B'_0 - 4)(x^{2/3} - 1)\right], \quad (1)$$

where $x = V_N/V$, B_0 is the isothermal bulk modulus at zero pressure, and B'_0 is the pressure derivative of B_0 evaluated at zero pressure [23]. The resulting values of the three parameters are $B_0 = 60.6 \pm 5.4$ GPa, $B'_0 = 4.1 \pm 0.3$, and $V_N/V_0 = 0.778(5)$. Here V_N/V_0 is the extrapolated volume of the $B8$ phase divided by the volume of the original wurtzite phase, both at zero pressure. The data points for the wurtzite phase were not adequate to make a meaningful two-variable fit. The volume change at 1 GPa is estimated to be about 22%.

Downloading data were obtained from the first experiment, in which the NiAs structure persisted all the way back to the point when the loading nut on the DAC was effectively loose. To further investigate this phenomenon, in the last experiment we loaded the cell to 5.6 GPa and started downloading with very small steps. To prevent the sample from possible exposure to air when the nut on the DAC becomes loose, we used Epoxy 709 adhesive to seal around the diamond anvil and the gasket in contact. All the downloading diffraction patterns index to the NiAs phase. At the end of downloading the pressure of the sample was measured at 0.4 GPa from the ruby fluorescence. We then annealed the cell at 100 °C for 10 h. The residual pressure in the sample dropped to about 0.2 GPa. The diffraction spectrum taken after the annealing proves the sample was still in the NiAs structure.

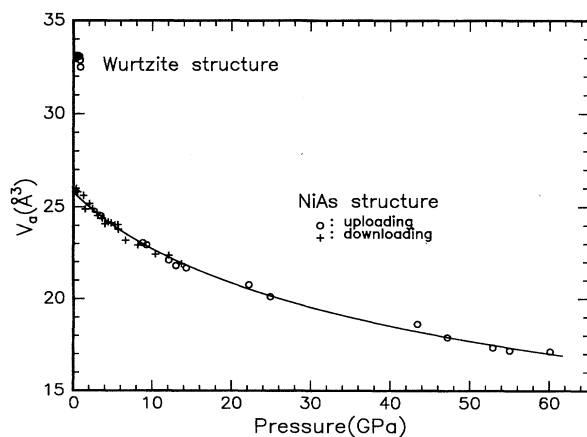


FIG. 2. Plot of atomic volume V_a of MgTe vs pressure P . Fit of the data points by the first-order Birch EOS for the NiAs phase is shown by the solid curve.

TABLE II. List of the observed and calculated interplanar spacings (d) and intensities (I) of the NiAs structure at 8.8 GPa.

(hkl)	d_{obs} (Å)	d_{calc} (Å)	I_{obs} (%)	I_{calc} (%)
(100)	3.498	3.489	2	3
(002)	3.299	3.282	8	9
(101)	3.080	3.081	72	68
(102)	2.393	2.390	49	45
(110)	2.014	2.014	100 ^a	100
(103)	1.859	1.856	43	43
(200)	N.A.	1.744	^b	2
(112)	1.715	1.717	40	28
(201)	1.683	1.686	23	32
(004)	N.A.	1.644	^b	10
(202)	N.A.	1.541	0	15
(104)	N.A.	1.487	0	2
(203)	1.366	1.365	3	14
(210)	N.A.	1.319	^b	2
(211)	1.292	1.293	11	22
(114)	1.271	1.272	5	20

^aThe integrated intensity of MgTe (110) is deconvoluted from that of Au(200) by subtracting the estimated intensity of Au(200) from the mixture. The estimation is based on the assumption that the intensity ratio of Au(111)/Au(200) remains roughly independent of pressure. This assumption is generally true through observation of diffraction spectra.

^bThe MgTe (200), (004), and (210) lines are unresolvable since they are overshadowed by stronger ones in their vicinity.

The transition sequence of phases for MgTe can be summarized as, on uploading, the transition from the wurtzite to NiAs structure occurs at $P \approx 1-3.5$ GPa; on downloading, the NiAs phase persists to pressure at least as low as 0.2 GPa. Therefore, the thermodynamic equilibrium transition pressure can be located only below 3.5 GPa and maybe even into the negative range, which means, the NiAs structure might be the thermodynamic stable phase at atmospheric pressure. This will be discussed further in the following paragraphs.

The NiAs phase of MgTe is not surprising as we recall MnTe is found in the NiAs structure at ambient conditions and the $3d$ electrons in the latter are usually considered as chemically inactive. It is also interesting to note that recent studies on AlAs [14] and AlP [24] show both transform from the zinc blende to the NiAs structure with large hysteresis in the transition pressure. However, this is the first example of a wurtzite to NiAs transition at high pressure among binary compounds.

Van Camp and Van Doren [9] did predict correctly that MgTe has the lowest total energy in the NiAs structure under pressures at least up to 60 GPa (which corresponds to $V/V_0 = 0.65$ from our EOS as their calculations extend to $V/V_0 = 0.60$). However, no theoretical calculations on the sixfold-to-eightfold structural transition for MgTe have been made. From the high-pressure behaviors of MgO, CaO, and CaTe, we expect that the transition pressure of MgTe from the NiAs phase to an eightfold coordinate structure, such as CsCl, would probably be much higher than 60 GPa. [Another transition sequence,

NiAs \rightarrow PH₄I(tetragonal) \rightarrow CsCl, which was found in BaO [25], is also possible.]

Now we return to the more intriguing question of which structure is indeed the thermodynamic stable phase at room temperature and pressure. Since nearly all approaches to make MgTe up to now necessarily involve high temperature of at least 700 °C, we would like to emphasize that it is *possible* that the wurtzite structure is stable only at high temperatures and, due to kinetic reasons, it remains metastable at room temperature, while the NiAs structure is the true stable phase at low temperature. The calculations by Yeh *et al.* [8] are consistent with this picture. They found -14 meV/atom as the energy difference for the NiAs relative to the wurtzite structure. From their calculations, we can obtain that at zero pressure, the cell volume ratio of NiAs to wurtzite structure is 77.3%, which is in good agreement with our experimental value of $V_N/V_0 = 77.8\%$. It is also consistent with the 22% volume collapse at 1 GPa. Although our annealing result is not sufficient for us to reach a conclusive judgement, it is an evidence in support of the theoretical studies.

The only exception which does not involve high temperatures is the molecular-beam epitaxy (MBE) growth of MgTe. As reported by Waag *et al.* [1], on the 200 °C CdTe (zinc blende) substrate, about 500 nm of MgTe film can be stabilized in the zinc blende structure before a relatively abrupt transformation to an apparent hexagonal polycrystalline structure occurs. It would be helpful if efforts are to be made to identify the crystal structure of the "bulklike" phase. Although the MBE growth is restricted by the congruent sublimation temperature condition (see, for example, Ref. [26]), it would be desirable to explore the possibility of lowering the growth temperature further. In that case the result of the structure determination of the bulklike specimen will be a strong indication of the stable phase.

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