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# Structural properties and phase transformations under pressure of XTe compounds (X = Be, Mg, and Ca): The role of the exchange–correlation potential

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ABSTRACT

We have performed first principles total energy calculations to investigate the structural properties and possible phase transitions under pressure of IIA–VI compounds: BeTe, MgTe and CaTe. We have considered the following possible structures: rock-salt, nickel arsenide, cesium chloride, zinc-blende, and in some cases wurtzite. Calculations are done using the periodic density functional theory. We employ the full potential linearized augmented plane wave method as implemented in the wien2k code. The exchange and correlation potential energies are treated according to the generalized gradient approximation (GGA) using the Perdew, Burke, Ernzerhof (PBE) parameterization, and the local density approximation (LDA). Our results show that the GGA calculations correctly predict the ground state structure of all three binary compounds: zinc-blende for BeTe, wurtzite/zinc-blende for MgTe, and rock-salt for CaTe. Under pressure, BeTe and MgTe transform to the nickel arsenide structure, while CaTe transforms from rock-salt to cesium chloride. Slightly different results are found using the LDA approximation. We discuss the role of the ionicity in the difference between the LDA and GGA results.


## 1. Introduction

The structural properties of Group IIA chalcogenides have attracted the attention of researchers, since some of these compounds have large band gaps and low dielectric constants, and therefore they may be used in blue-wavelength optics and high temperature electronics [1]. In particular, the atomic structure of Group IIA tellurides and their phase transitions under pressure have been investigated extensively. It has been found experimentally that zinc-blende is the ground state configuration of BeTe. Also it has been shown the existence of a first order transition between zinc-blende and nickel arsenide phases at a pressure of $35 \pm 5$ GPa [2]. First principles calculations using the local density approximation [3] have corroborated the zinc-blende geometry as the ground state for this compound (although they did not considered the wurtzite structure), and the transformation to a nickel arsenide structure. The situation is more complicated for MgTe: experimental studies [4,5] on the atomic structure have shown the wurtzite phase to be the ground state configuration. However, first principles calculation using the LDA [6] predicted the ground state of MgTe to be the NiAs structure at $T = 0$ K. Li et al. have performed studies on the pressure dependence and found a wurtzite to NiAs transition in the 1–3.5 GPa range [7]. The NiAs structure persisted after unloading to the lower pressure of 0.2 GPa. The authors speculated that NiAs may be the ground state of MgTe. Recent first principles calculations [8] confirmed that the ground state is NiAs when using LDA, but they found the hexagonal wurtzite phase to be the ground state when using the generalized gradient approximation (GGA). Experimental investigations of the CaTe atomic structure [9,10] have yielded the rock-salt phase as the ground state configuration with a phase transition to CsCl structure at a pressure of 33 GPa. We are not aware of any first principles calculations of this material.

As explained in the past paragraph, the three Group IIA–Group VI compounds change from the BeTe in the more open wurtzite phase to CaTe in the rock-salt structure. MgTe is intermediate and therefore, first principles calculations predict different phases depending on the approximation of the exchange–correlation energy. The LDA uses the exchange–correlation density of the uniform electron gas of the same charge density at every point in the system regardless of the inhomogeneity of the real charge density. The general gradient approximation (GGA) additionally uses the gradient of the charge density to correct for this deviation, and therefore it is thought to be

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more accurate. However, some exceptions of this rule are found in systems where the bonding is intermediate between ionic and covalent [11]. A similar trend has been observed for group IIB–group VI compounds: for example ZnO crystallizes in the wurtzite structure [12], while the ground state of CdO is rock-salt [13]. Also, wurtzite and zinc-blende are structurally similar, they differ only by the stacking in the (111) direction, and therefore energy differences are very small. A similar situation occurs between rock-salt and nickel arsenide phases. Therefore, we believe it is interesting to study these three compounds using the most popular approximations for the exchange–correlation. In this paper, we report first principles total energy calculations to investigate the structural properties of CaTe, BeTe, and MgTe using the LDA and GGA (with the Perdew, Burke, and Ernzerhof scheme [14]). Our results show that the GGA calculations correctly predict the ground state structure of all three binary compounds: zinc-blende for BeTe, wurtzite/zinc-blende for MgTe, and rock-salt for CaTe. Structural parameters are in good agreement with available experimental data. Under pressure, BeTe and MgTe transform to the nickel arsenide structure, while CaTe transforms from rock-salt to cesium chloride. Slightly different results are found using the LDA. The paper is organized as follows: In Section 2 we describe the method. In Section 3 we present the results, in Section 4 we discuss the differences between the LDA and GGA results, and in Section 5 we make conclusions.

## 2. Computational technique

We perform first principles total energy calculations to study the atomic configurations of BeTe, MgTe, and CaTe in the following geometries: rock-salt, NiAs, CsCl and zinc-blende. In addition, for BeTe and MgTe we have also considered the wurtzite structure. Calculations are done within the periodic density functional theory (DFT) [15,16]. We apply the full potential linearized augmented plane wave (LAPW) approach as developed in the wien2k code [17]. The exchange and correlation potential energies are treated within the generalized gradient approximation (GGA) within the PBE [14] and the local density approximation (LDA) using the Perdew and Wang [18] fit to the Monte-Carlo simulations of Ceperley and Alder [19]. For the muffin tin radii we have used the following values: 1.4 for Be, 1.6 for Mg, 2.2 for Ca and 2.1 for Te, and 8 for the RKmax value. The numbers of integrating points over the irreducible part of the first Brillouin zone that we have used are: 72, 42, 84, 91 and 70 *k*-points for the rock-salt, NiAs, CsCl, zinc-blende and wurtzite structures, respectively. We have carefully tested the convergency of the *k*-points, larger number of *k*-points made negligible differences.

## 3. Results

### 3.1. BeTe

Fig. 1a and b shows the calculated total energy for BeTe as a function of volume, $E = E(V)$. Symbols represent the calculated

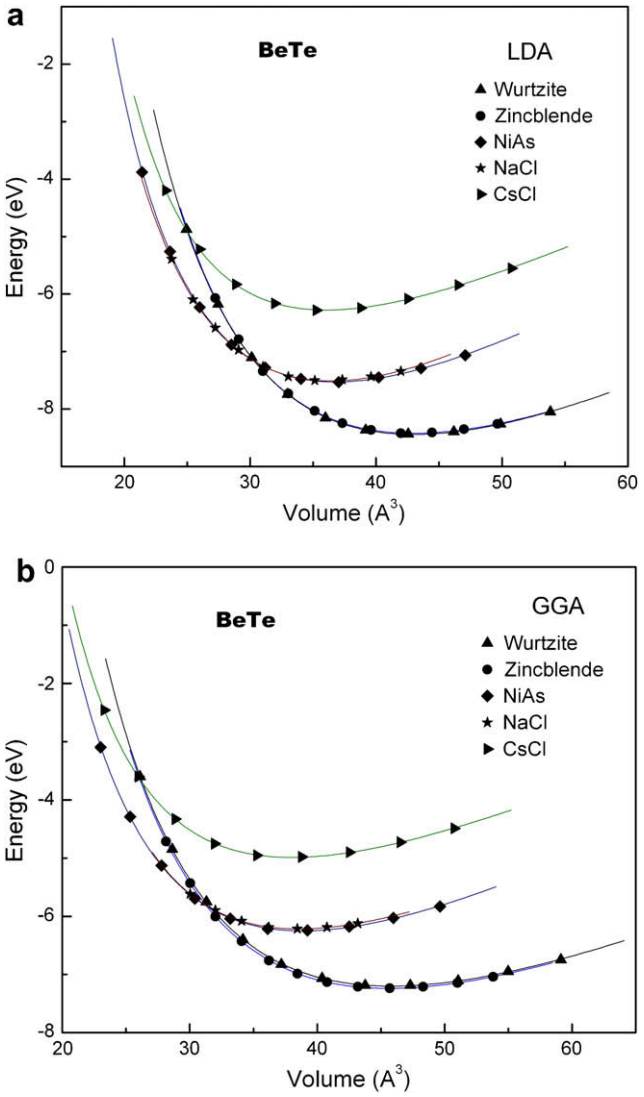


**Fig. 1.** Total energies (per unit formula) as function of volume for BeTe using (a) the LDA and (b) the GGA.

energies and solid curves are obtained by fitting the calculated data to the Murnaghan [20] equation of state for each phase. In Fig. 1a, the exchange and correlation energies are treated within the local density approximation (LDA), and in Fig. 1b, within the generalized gradient approximation (GGA). Five structures have been considered: zinc-blende (circles), wurtzite (triangles), rocksalt (stars), NiAs (rhombuses), and CsCl (rotated triangles). Energies and volumes are per single BeTe formula unit. According to the LDA calculations, the lowest minimum energy corresponds to the

**Table 1**
Calculated structural parameters for BeTe. $u$ is an internal parameter of the wurtzite structure, and $E_0$ is the difference between the total energy of the compound and the energy of the individual atoms. Values in parenthesis are from Ref. [3].

| Structure | Rock-salt | | NiAs | | CsCl | | Zinc-blende | | | Wurtzite | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | GGA | LDA | GGA | LDA | GGA | LDA | GGA | LDA | Exp. | GGA | LDA |
| $a$ (Å) | 5.36 | 5.26 (5.252[b]) | 3.89 | 3.80 (3.774[b]) | 3.36 | 3.30 (3.314[b]) | 5.67 | 5.56 (5.531[b]) | 5.617[a] | 4.07 | 3.91 |
| $c/a$ | | | 1.53 | 1.55 (1.556[b]) | | | | | | 1.56 | 1.67 |
| $u$ | | | | | | | | | | 0.38 | 0.37 |
| $V$ (Å$^3$) | 38.56 | 36.42 | 38.85 | 36.80 | 38.02 | 36.04 | 45.63 | 42.96 | | 45.81 | 42.99 |
| $B_0$ (GPa) | 66.7 | 82.5 (79.2[b]) | 66.4 | 75.7 (76.6[b]) | 59.7 | 67.4 (69.9[b]) | 56.1 | 62.4 (70.6[b]) | | 55.6 | 64.4 |
| $E_0$ (eV) | −6.22 | −7.52 | −6.25 | −7.53 | −4.99 | −6.28 | −7.24 | −8.43 | | −7.20 | −8.45 |

[a] Ref. [2].
[b] Ref. [3].