First principles study of structural, electronic and optical properties of polymorphic forms of Rb_2Te

S.M. Alay-e-Abbas [a], A. Shaukat [b],*

[a] Department of Physics, GC University Faisalabad, Allama Iqbal Road, Faisalabad 38000, Pakistan
[b] Department of Physics, University of Sargodha, Sargodha 40100, Pakistan

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ABSTRACT

First-principles density functional theory calculations have been performed for structural, electronic and optical properties of three polymorphic forms of rubidium telluride. Our calculations show that the sequence of pressure induced phase transitions for Rb_2Te is $Fm\overline{3}m \rightarrow Pnma \rightarrow P6_3/mmc$ which is governed by the coordination numbers of the anions. From our calculated low transition pressure value for the $Fm\overline{3}m$ phase to the $Pnma$ phase transition of Rb_2Te, the experimentally observed meta-stability of $Fm\overline{3}m$ phase at ambient conditions seems reasonable. The electronic band structure has been calculated for all the three phases and the change in the energy band gap is discussed for the transitioning phases. The energy band gaps obtained for the three phases of Rb_2Te decrease on going from the meta-stable phase to the high-pressure phases. Total and partial density of states for the polymorphs of Rb_2Te has been computed to elucidate the contribution of various atomic states on the electronic band structure. Furthermore, optical properties for all the polymorphic forms have been presented in form of the complex dielectric function.

1. Introduction

The large energy band gap of alkali-metal chalcogenide compounds is an important characteristic of these materials that make them technologically useful and interesting as functional materials. These compounds are a good example of homologous series of solids that have predictable physical and physiochemical properties. Rubidium telluride, a unique member of this family, has found potential applications as hybrid photodiode (HPD) [1,2] for astroparticle physics. In addition to that, its use as a precursor in the production of the Rb_2Te/Te fluxes for the development of quaternary metal tellurides [3] has earned Rb_2Te academic as well as technological interest. The uniqueness of Rb_2Te among other group-IA-VI binary compounds can be attributed to the fact that unlike the Li, Na and K tellurides in particular and chalcogenides in general that crystallize stably into a anti-CaF_2 type structure [4,5], rubidium telluride is metastable in anti-CaF_2 (ω-Rb_2Te, space group # 225, $Fm\overline{3}m$) type structure and transforms to the anti-$PbCl_2$ (α-Rb_2Te, space group # 62, $Pnma$) type and further to the Ni_2In (β-Rb_2Te, space group # 194, $P6_3/mmc$) type structure under application of temperature as well as pressure. The atomic positions for the

ω-Rb_2Te phase are Rb (1/4; 1/4; 1/4) and Te (0; 0; 0) and the experimental lattice constant at room temperature is $a = 8.4902$ Å [6]. In case of the orthorhombic α-Rb_2Te, the experimental atomic positions of Rb(1), Rb(2) and Te atoms at room temperature are (0.0271; 1/4; 0.1784), (0.1534; 1/4; 0.5728) and (0.2483; 1/4; 0.8860), respectively, and the lattice constants are $a = 8.9660$ Å, $b = 5.5715$ Å and $c = 10.9543$ Å [6]. The atomic positions of the hexagonal β-Rb_2Te are Rb(1)(0; 0; 0), Rb(2)(1/3; 2/3; 3/4), Te(1/3; 2/3; 1/4) and the experimental lattice constants available in literature at $T = 680$ °C and $P = 2.04$ GPa are $a = b = 6.1110$ Å, $c = 9.1900$ Å [6] and $a = b = 5.9320$ Å, $c = 7.5820$ Å [7], respectively.

Due to highly unstable and air-sensitive nature of Rb_2Te, researchers have either failed [8] or left unable to provide useful information [9,10] on solid-state properties of this compound. The first successful X-ray powder diffraction studies and differential thermal analysis (DTA) for Rb_2Te carried out by Stöwe and Appel [6] revealed three polymorphic forms of this compound. Their studies show that Rb_2Te is metastable in anti-CaF_2 type structure and undergoes an irreversible phase transformation into the orthorhombic anti-$PbCl_2$ type crystal structure upon warming which can undergo a further reversible phase transformation into the hexagonal Ni_2In type structure at $T = 660$ °C. This transition series is the most typical variant of atomic coordinations observed in ionic compounds of the form AX_2 [11,12] and A_2X [13–15], that is, the anti-CaF_2 type structure with coordination numbers (CNs) = 8, the

* Corresponding author. Tel.: +92 48 9230618; fax: +92 48 9230671.
  E-mail address: schaukat@gmail.com (A. Shaukat).

anti-PbCl$_2$ type structure with CNs = 9 and the Ni$_2$In type structure with CNs = 11. However, the uncommon and striking feature of this transition series in Rb$_2$Te is that in above mentioned A$_2$X and AX$_2$ compounds it is only pressure induced, on the other hand, for rubidium telluride this transition series is temperature as well as pressure induced. For this reason Stöwe [7] extended the study on Rb$_2$Te by carrying out high-pressure diamond anvil cell (DAC) measurements along with *ab-initio* calculations in the framework of density functional theory (DFT) using pseudopotentials method. The pressure-induced experimental and theoretical phase transformation and the corresponding transition pressures (P_T) were found to be in good agreement with each other. Moreover, a series of measurements in the modified Mao-Bell type DAC also revealed that β-Rb$_2$Te does not undergo any further phase transformation up to a pressure of 10 GPa. The pressure induced α-Rb$_2$Te to β-Rb$_2$Te transformation is related by a group–subgroup relation that enables one to describe the Ni$_2$In type structure within the symmetry framework of anti-PbCl$_2$-type structure and the transition between the two can be characterized as continuous in real space coordinates (1st Landau Criterion) [7].

The experimental and theoretical findings mentioned above clearly indicate that pressure is certainly a critical parameter for structural stability of rubidium telluride; however no studies have been performed for the electronic and optical properties of Rb$_2$Te in its polymorphic forms under the application of pressure, to the best of our knowledge. Since the main advantage of modern theoretical condensed matter physics lies in the fact that it can be used to predict the possibility of existence of stable and metastable structures and can also be effectively utilized to provide a *priori* information of important solid-state properties of materials. In this paper we investigate the electronic and optical properties of three possible phases of Rb$_2$Te using full relativistic electronic structure calculations. To accomplish this task, we first confirm the phase transformations of Rb$_2$Te observed in previous studies and compute the ground-state structural properties of the polymorphic forms of Rb$_2$Te for comparison with available data. Afterward, the features of the electronic band structures for the three possible phases of Rb$_2$Te and their corresponding optical properties have been calculated using the theoretically calculated ground-state values of structural parameters utilizing the most successful first-principles technique, i.e., full potential linear augmented plane-wave (FP-LAPW) method. The results for electronic and optical properties of the polymorphic modifications of Rb$_2$Te presented in this work may prove useful for future development of rubidium telluride based optoelectronic devices.

2. Computational methods

We have performed the calculations for the three phases of rubidium telluride, ω-Rb$_2$Te, α-Rb$_2$Te and β-Rb$_2$Te, respectively, using the FP-LAPW method in its density functional theory formalism as implemented in the WIEN2K code [16]. For the FP-LAPW calculations reported in this work, the exchange and correlation effects have been treated by the generalized gradient approximation (GGA) functional proposed by Wu and Cohen (WC-GGA) [17]. A muffin-tin model for the crystal potential has been assumed and same radius R_{MT} (Rb = 2.5 *a.u* and Te = 2.7 *a.u*) of muffin-tin spheres has been used for all calculations to increase the reliability of calculations for different structure types. Linear combination of radial solution of the Kohn–Sham equation times the spherical harmonic has been utilized inside the non-overlapping muffin-tin spheres and the energy threshold between the core and valence states has been set at −6.0 Ry. The maximum value of angular momentum, I_{MAX}, for the wave function expansion inside the atomic spheres has been taken at 10. In the interstitial

region plane-wave basis sets have been utilized and plane-wave cut-off value of $K_{MAX} \times R_{MT} = 7$ has been used to control the size of basis set for wave functions. 2000 **k**-points have been generated in the whole Brillouin Zone that yielded a mesh of 72, 270 and 120 **k**-point in the corresponding irreducible wedge for ω-Rb$_2$Te, α-Rb$_2$Te and β-Rb$_2$Te, respectively.

3. Structural properties

The minimum total energy of the unit cell for a number of different volumes of each crystal structure has been calculated. In the self-consistent cycle for ω-Rb$_2$Te and β-Rb$_2$Te phases the convergence criteria was only specified for energy and charge due to symmetry without atomic positions in these structures, however, for the β-Rb$_2$Te phase the c/a ratios have also been optimized for each crystal volume and the minimum total energy has been obtained at these optimized c/a ratios. In the case of the α-Rb$_2$Te phase we have optimized c/a and b/a ratios for each volume of the unit cell by relaxing all the internal atomic coordinates until forces on every atom were below a tolerance value of 1 mRy/a.u. The ground-state structural properties presented in Table 1 have been calculated by fitting Murnaghan equation of state (EOS) [18] to the minimum total energy/formula unit versus volume/formula unit curves presented in Fig. 1. It is clear that our calculated values of lattice parameters for the ω-Rb$_2$Te and α-Rb$_2$Te phases agree very well with the experimental data as well as with theoretical results. The value of pseudopotential DFT lattice parameter presented in Table 1 for ω-Rb$_2$Te has been calculated from the unit cell volume data of Ref. [7], since the author of this paper has somehow confused the nearest–neighbor distances of FCC lattice ($a_o/\sqrt{2}$) at various pressures with the lattice parameters (e.g. $a_o = 6.009$ Å at 0 GPa as lattice constant for ω-Rb$_2$Te in Ref. [7]). Our calculated a_o, c_o and b_o values for the α-Rb$_2$Te phase are in excellent agreement with experimental data because the internal atomic coordinates obtained in this work using FP-LAPW method are in much better agreement (Table 1) with experimental data at room temperature as compared to the pseudopotential method results. Because of unavailability of experimental data for β-Rb$_2$Te at zero pressure we compare our theoretically calculated ground-

Table 1
Calculated lattice parameters (Å), bulk modulus B_o (GPa) and its pressure derivative B' for the three phases of Rb$_2$Te and the internal atomic coordinates for α-Rb$_2$Te at zero pressure along with available experimental and theoretical data.

Phases of Rb$_2$Te		Present work	Experimental	Other theoretical works[a]
ω-Rb$_2$Te ($Fm\overline{3}m$)	a_o	8.4744	8.4900[a]	8.4980
	B_o	11.8200	–	–
	B'	4.1437	–	–
α-Rb$_2$Te ($Pnma$)	a_o	8.8920	8.9598[a]	9.1010
	b_o	5.5224	5.5675[a]	5.3420
	c_o	10.8582	10.9463[a]	10.9650
	B_o	10.1817	–	–
	B'	3.9565	–	–
	xRb(1)	0.02713	0.0271 (3)[b]	0.02735
	xRb(2)	0.15357	0.1534 (2)[b]	0.14601
	xTe	0.24842	0.2483 (2)[b]	0.24847
	zRb(1)	0.17840	0.1784 (2)[b]	0.17101
	zRb(2)	0.57275	0.5728 (2)[b]	0.57139
	zTe	0.88545	0.8860 (1)[b]	0.88475
β-Rb$_2$Te ($P6_3/mmc$)	a_o	6.0266	5.9720 ($P = 1.30$ GPa)[a]	6.0640
	c_o	7.9093	7.7280 ($P = 1.30$ GPa)[a]	8.0190
	B_o	12.4370	–	–
	B'	3.8123	–	–

[a] Ref. [7].
[b] Ref. [6].