Ba₂TeO: a new layered oxytelluride

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Abstract

Single crystals of the new semiconducting oxytelluride phase, Ba₂TeO, were synthesized from barium oxide powder and elemental tellurium in a molten barium metal flux. Ba₂TeO crystallizes in tetragonal symmetry with space group *P4/nmm* (#129), $a = 5.0337(1)$ Å, $c = 9.9437(4)$ Å, $Z = 2$. The crystals were characterized by single crystal x-ray diffraction, heat capacity and optical measurements. The optical measurements along with electronic band structure calculations indicate semiconductor behavior with a band gap of 2.93 eV. Resistivity measurements show that Ba₂TeO is highly insulating.

1. Introduction

Oxychalcogenides make up an active field of research, as these materials show promise in a variety of fields, such as, e.g., optoelectronics [1, 2], superconductors (see, for instance the review by Johnston [3] and references therein), and more recently, as thermoelectrics [4-7]. Another area in which oxychalcogenides have been extensively investigated is their use as transparent conductors and semiconductors [8-11], with the layered copper-based oxychalcogenides standing out [12-22]. Many of the interesting properties of the

oxychalcogenides stem from their parent oxide and chalcogenide phases, with structural motifs still present as modified arrangements in the resulting oxychalcogenides.

Among semiconducting oxychalcogenides, oxysulfides and oxyselenides have been extensively investigated, in contrast to the oxytellurides. Tellurates and tellurites, tellurium-based compounds containing cationic $\text{Te}^{4+/6+}$ present as TeO_4^{2-} or TeO_4^{4-} anions, have been studied extensively [23-25], as well as semiconducting tellurides (compounds with anionic Te^{2-}) [26-28]. Oxytellurides, on the other hand, are rarer, with uranium oxytellurides UOTe [29, 30], $\text{U}_2\text{O}_2\text{Te}$ [31], and $\text{U}_4\text{O}_4\text{Te}_3$ [30, 32, 33] extensively studied. Furthermore, the physical properties of a number of the lanthanide oxytellurides $\text{Ln}_2\text{O}_2\text{Te}$ have also been investigated [34, 35]. More recently, a new layered oxytelluride, $\text{Ba}_3\text{Yb}_2\text{O}_5\text{Te}$, has been discovered [36].

The complex orbital hybridizations in anion-ordered multinary crystals such as oxytellurides can give rise to properties that differ vastly from the respective tellurides and oxides. Here, we report on the synthesis and property measurements of a new layered oxytelluride, Ba_2TeO , comprised of alternating puckered BaTe and BaO layers. Optical property measurements and theoretical calculations show Ba_2TeO to be a semiconductor with a band gap of 2.93 eV.

2. Experimental and computational methodology

The Ba_2TeO crystals were prepared from a barium metal flux, with 1 mmol of BaO and elemental Te for every 20 mmol of Ba metal. The starting materials were sealed in a stainless steel crucible using an arc welder under inert (argon) atmosphere in a glovebox. The steel crucibles were subsequently sealed in quartz tubing under vacuum. The sample was heated to 1000 °C over 10 hours, soaked at 1000 °C for 20 hours, and cooled to 820 °C over 50 hours. At 820 °C, the ampoules were removed from the furnace and centrifuged while the flux was still molten, in order to separate the flux from the crystals that formed. Large single crystal platelets with dimensions up to several millimeters were obtained in this way. The Ba_2TeO crystals had a metallic lustre with dark greyish to black appearance and were relatively brittle and tended to exfoliate and cleave easily. Crystals decomposed in the ambient at a moderate rate. To maintain sample integrity, all crystals used for subsequent analysis were handled and stored under inert atmosphere at all times possible.

Elemental analysis using EDS in a JEOL 5900 scanning electron microscope confirmed the stoichiometry of Ba₂TeO having a molar Ba:Te ratio of 2:1 across varying locations on multiple single crystals to within 5 at.% deviation.

The Ba₂TeO crystals were structurally characterized by single crystal x-ray diffraction (XRD) with an Oxford-Diffraction Xcalibur2 CCD system using graphite-monochromated MoK α radiation. Samples were suspended in Paratone-N oil in a cryoloop, and cooled with an Oxford-Diffraction Cryojet to a temperature of 200 K. Reflections were recorded, indexed and corrected for absorption using the Oxford-Diffraction CrysAlisPro software [37], and subsequent structure determination and refinement was carried out using CRYSTALS [38], employing SIR92 [39] to solve the crystal structure. The data quality allowed for a full matrix refinement against F^2 , with anisotropic thermal displacement parameters of all atoms in the structure. A CIF has been deposited with the FIZ-Karlsruhe (ICSD #428396) [40].

A Quantum Design PPMS system was used to measure the zero-field heat capacity between 2 K and room temperature, with crystals embedded in grease. Electrical resistivity was measured using 4-point contacts on samples of various thickness, but all samples studied were found to be highly resistive.

Optical absorption spectroscopy was performed on single crystal samples. Thin layers of Ba₂TeO crystals were obtained by exfoliating large single crystals with adhesive tape. The process was repeated until the samples became visibly transparent. The thin layer was then mounted on a copper pinhole 600 μ m in diameter using the adhesive tape as substrate; a reference pinhole of 600 μ m was prepared using the same adhesive tape. The sample and reference were mounted in a cylinder that was sealed with fused silica windows on either end, and purged under a constant flow of nitrogen to protect the sample from oxidation. The spectrum was measured using an Ocean Optics LS-1 light source and USB2000 spectrometer in the wavelength range from 450 to 1000 nm. For UV-VIS absorption between 300 and 500 nm, a deuterium light source coupled with an Acton SP2300 spectrometer and back-illuminated, liquid nitrogen cooled CCD were used.

First-principle calculations of the electronic structure and optical properties, based on density functional theory (DFT) [41, 42], were carried out using the WIEN2k code [43], which employs the full-potential linearized augmented plane-wave and local orbitals (FP-LAPW+lo) method [44]. In order to obtain a more accurate band gap, the modified Becke-Johnson (mBJ)

method [45] was used for the exchange-correlation potential. The LAPW sphere radii employed were 2.6 Bohr for both barium and tellurium, and 2.0 Bohr for oxygen. The cut-off parameter for the plane wave basis was $R_{\min}K_{\max}=7$, where $R_{\min}=2$ Bohr is the smallest sphere radius. The convergence was tested and an $8\times 8\times 8$ k-mesh for band structure calculations and a $16\times 16\times 16$ k-mesh for optical properties calculations was employed. Because of the relatively heavy elements barium and tellurium, spin-orbit coupling was also included.

3. Results and Discussion

The growth of single crystalline Ba_2TeO so far is possible in the molten metal flux only, as presented in this report. Direct solid state reactions produced only the binary compounds BaTe and BaO, but not Ba_2TeO . The Ba metal flux, in this case, allows simultaneous solubility of oxygen as well as Te and enables the formation of Ba_2TeO at moderate temperatures.

3.1 Structure and Strain

The Ba_2TeO single crystal grew in a structure with tetragonal symmetry and space group $P4/nmm$ (#129). Results of the XRD refinement are summarized in Table 1, along with selected interatomic distances and angles.

Table 1

Single crystal x-ray diffraction data and collection parameters (collected at 200 K), atom positions, and selected distances and angles.

Formula	Ba_2TeO
Formula weight	418.26 g/mol
Space group	$P4/nmm$ (#129) origin 2
Cell parameters	$a = 5.0337(1) \text{ \AA}$, $c = 9.9437(4) \text{ \AA}$
Volume	$251.96(2) \text{ \AA}^3$
Z	2
$D_{\text{calc.}}$	5.513 g/cm^3
μ	21.029 mm^{-1}
Data collection range	$4.099^\circ < \theta < 66.506^\circ$
Reflections collected/independent	11169/1359
Parameters refined	13
R_1 , wR_2	0.0751^a , 0.0769^b
Goodness-of-fit	1.2831

Refined atomic positions							Ideal atomic positions			
Atom	Site	Occ.	x	y	z	$U_{eq} (\text{\AA}^2)$	Atom	x	y	z
Ba1	2c	1	3/4	3/4	0.16449(6)	0.0110(2)	Ba1	3/4	3/4	1/6
Ba2	2b	1	1/4	3/4	1/2	0.0109(2)	Ba2	1/4	3/4	1/2
Te	2c	1	1/4	1/4	0.20113(7)	0.0115(2)	Te	1/4	1/4	1/6
O	2c	1	3/4	3/4	0.4110(8)	0.0118(2)	O	3/4	3/4	1/2

Selected distances (Å)

Ba1 – O	2.451(1)
Ba2 – O	2.668(1)
Ba1 – Te, along [110]	3.578(1)
Ba1 – Te, along [001]	3.636(1)
Te – O	3.857(1)

Selected angles (°)

Ba1 – Te – Ba1, along [110]	168.31(3)
Ba2 – O – Ba2, along [100] or [010]	141.25(1)
Te – Ba1 – O, along [001]	180.00

$$^a) R_1 = \Sigma \|F_o\| - \|F_c\| / \Sigma \|F_o\|.$$

$$^b) wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)]^{1/2}, w = [\sigma^2(F_o^2) + (A \cdot p)^2 + B \cdot p]^{-1}; p = (F_o^2 + 2F_c^2)/3; A = 0.0067, B = 0.$$

The structure of Ba₂TeO is a combination of alternating layers of BaTe (containing Ba1) and BaO (containing Ba2), stacked in the *c* direction (see Figure 1). The *parent* BaTe and BaO phases both crystallize in the NaCl (rocksalt) structure type. The very differing bonding distances present in BaO and BaTe are accommodated in Ba₂TeO by a two-dimensional layering of its structure, and the ratio of the two bond distances Ba–O and Ba–Te needs to be within an acceptable range in regard to lattice mismatch.

The structure of Ba₂TeO can be “built up”, or obtained, by starting from a simpler, “ideal” structure, followed by a transition towards the actual structure by accommodation of structural strain via atom displacements. An ideal stacking arrangement that accommodates layers with different internal bond distances is a tetragonal unit cell where the long bonds (Ba–Te) are aligned with the [110] direction and the short bonds (Ba–O) along the [100] direction. For this arrangement, the ratio between the two bond distances should be $d(\text{Ba} - \text{O})/d(\text{Ba} - \text{Te}) = 1/\sqrt{2}$. For a simple arrangement of one BaTe layer and one BaO layer, there can be two different types of contacts along the *c*-axis: either [Ba–Ba]_n contacts, or [Ba–

Te]_n contacts. If two BaTe layers alternate with one BaO layer, [BaTe–Ba₂O₂–BaTe]_n stacking forms along the *c*-axis.

Figure 1: (a) Unit cell of Ba₂TeO displaying anisotropic displacement ellipsoids with 95% probability. (b) and (c) Local coordination of Ba1 and Ba2, respectively, along with selected bond distances.

Using space group *P4/nmm* (#129), atom positions for the ideal structure can be obtained and are listed in Table 1. This ideal structure, combining NaCl-type layers, is illustrated in Figure 2a. Using a unit cell parameter of $a=5$ Å, the in-plane Ba–Te distance in this structure is $5/\sqrt{2} \approx 3.54$ Å, in agreement with the distance of approximately 3.5 Å found in rocksalt type BaTe [25]. For the ideal, flat BaO layer, the Ba–O distance in this arrangement is then 2.5 Å, whereas rocksalt type BaO shows a distance of approximately 2.75 Å [25], a 9% mismatch. In this arrangement, the Ba–Te bond dominates the structure, and the Ba–O bond is in strong compression, with structural relaxation expected, where either the oxygen atom or the barium atom moves out of the plane parallel to the *c*-axis towards a BaTe layer. With no apical atom in the Ba2 coordination, the oxygen atom moving towards the BaTe layer will induce stronger bonding between the layers, rather than if the barium atom would move. Half of the oxygen

atoms move up towards Ba1 in the BaTe layer above, while the other half move down towards the Ba1 in the BaTe layer below, producing a puckered BaO layer, illustrated in Figure 2b. Comparing this layer to the corresponding layer in a high pressure phase of BaO (HP-BaO), related to the PbO structure [46], it is immediately seen that in HP-BaO, the roles of Ba and O are reversed. In the case of Ba₂TeO, the in-plane strain produces *inverse* PbO-type layers, since the oxygen atoms move, while the barium atoms remain in the original plane. Finally, the BaTe layer slightly puckers so that the fully relaxed structure connects the BaTe layers with the BaO layers via a short Ba–O bond, illustrated in Figure 2c.

The *interlayer* Ba1–O bond is short, at 2.451 Å, but several compounds exist with similarly short Ba–O bonds, e.g., Ba₂FeBrO₃ [47], Ba₃Lu₄O₉ [48], Ba₂ZrO₄ [49], and the high pressure phase of BaO [50] (see Ref. [25] for more examples). The *intralayer* Ba2–O bond is 2.668 Å, within 3% of the Ba–O distance in rocksalt-type BaO. The displacement of oxygen out of plane is clearly manifest in the Ba2–O–Ba2 angle of 141° (as compared to the ideal rocksalt angle of 180°), while the puckering of the BaTe layer results in a Ba1–Te–Ba1 angle of 168° (selected distances and angles are listed in Table 1). The bond valence sum (BVS) of Ba1 is 1.902, indicating underbonding of the barium in the BaTe layer, despite the short interlayer Ba1–O bond. The Ba2 in the BaO layer is similarly underbonded as indicated by its BVS of approximately 1.864, even though four Te ions were included in the calculation: two from the BaTe layer above and two from the BaTe layer below. This underbonding is most likely due to the lack of apical atoms in the Ba2 coordination.

Figure 2: (a) Ideal structure of layered BaO and BaTe, (b) structure where the oxygen atoms are displaced, and finally (c) the actual structure of Ba₂TeO with puckered BaTe layers.

The structure of Ba₂TeO is related to the “filled” PbFCl type [51], although it would rather be a “filled” *anti*-PbFCl type since the atomic positions of Pb and Cl are occupied by the anions Te and O, respectively, while Ba2 occupies the position of the F ion. The “filling” atom would then be Ba1, in a position different as compared to ZrSiCuAs, also a filled PbFCl-type structure.

With an origin change of the unit cell, the structure of Ba₂TeO maps onto the LuNiBC structure [52] (isostructural with ScCoC₂ [53]), which consists of inverse PbO-type layers of Ni₂B₂ separated by stacked NaCl-type LuC layers. The structural difference between Ba₂TeO and LuNiBC lies in the rocksalt layers: in LuNiBC, LuC is arranged in such a way that the “anionic” carbons form the short bonds to the inverse PbO-type layer (C–B bond), while in the case of Ba₂TeO it is the cationic Ba1 atoms that participate in the short interlayer bonding. Switching Ba1 and Te would make Ba₂TeO isostructural to LuNiBC, but with short Te–O bonds. However, refining such an arrangement results in a wR_2 that is approximately 10% higher, confirming our initial structure.

Other possible 2-1-1 alkaline earth oxychalcogenide phases may also be stable, but in the case of Ba₂SO and Ba₂SeO, the shorter Ba–S/Se distance would put an additional compression on the

Ba–O distances. Indeed, synthesis using the same method produced only the binaries. Therefore, with the exception of Ba₂TeO, no other barium oxychalcogenide phase is expected to exist. Replacing barium with the smaller alkaline earth metals Sr, Ca, and Mg, may produce potential candidates for isostructural phases, and a continued search for a synthesis route is ongoing.

3.2 Density of states

The density of states plot in Figure 3 shows a band gap of approximately 2.5 eV, indicating that Ba₂TeO is a semiconductor. The valence states in the region -2.2 – 0 eV are mainly occupied by the Te 5*p* and O 2*p* states, with the Te 5*p* dominating the valence band edge near zero. The relatively narrow valence band width is an indication of weak interactions between the Te anions, which may cause heavy electron effective masses. A small overlap between Te 5*p*/O 2*p* orbitals and Ba 5*d* orbitals in the region between -2 and 0 eV indicates hybridization between these orbitals, generating a weak covalency. Nominally, Ba²⁺ has unoccupied 5*d* orbitals, while Te²⁻ has fully occupied 5*p* orbitals. In this compound there is a clear mixing of Ba 5*d* states in the occupied states, indicative of this covalency. The conduction bands in the region 2.5–12 eV are dominated by the two inequivalent Ba 5*d* states with small amounts of Te 5*p* and O 2*p* antibonding states. Furthermore, the Te 5*s*² orbitals (not shown here) are quite localized from -9.2 to -8.5 eV, with little Ba 5*p* orbitals overlap.

Figure 3: Total and partial density of states.

3.3 Heat Capacity

The temperature dependence of heat capacity for a 4 mg sample of Ba_2TeO is shown in Figure 4. The small inset (a) illustrates the low-temperature region, plotted as C_p/T vs T^2 . This low temperature behavior is described by $C_p/T = \beta T^2$, since the electronic contribution to the heat capacity is zero, consistent with semiconducting Ba_2TeO . The low temperature data yields the lattice contribution $\beta \approx 2.0 \pm 0.3 \text{ mJ/mol} \cdot \text{K}^4$, and the Debye temperature θ_D can be estimated via the relation [54, 55]

$$\theta_D = \sqrt[3]{\frac{12\pi^4 Rn}{5\beta}}.$$

Here, n denotes the number of atoms per formula unit ($n=4$ for Ba_2TeO) and R the molar gas constant, yielding a Debye temperature of $\theta_D \approx 158 \pm 8 \text{ K}$.

Figure 4: Temperature dependence of the heat capacity of Ba_2TeO , obtained at zero applied field. The solid blue line is a fit to a combined Debye-Einstein model, while the dashed red and dotted green are fits to the separate Debye and Einstein models, respectively. Inset (a) displays the low temperature linearity of C_P/T vs T^2 . Inset (b) is a close-up of the low temperature region with the three different models.

To gain further insight in the lattice dynamics, the full temperature range of the measured heat capacity is considered. A Debye or single Einstein mode model cannot adequately describe the temperature dependence of the heat capacity, as is clearly seen in the fit of the data to the two models (Figure 4 and inset (b) for the low temperature region). A combined model, on the other hand, including the contribution of a Debye and an Einstein model, describes the heat capacity adequately: $C_P = C_D + C_E$ with

$$C_P = c_D \left(\frac{T}{\theta_D} \right)^3 \int_0^{\theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx + c_E \left(\frac{\theta_E}{T} \right)^2 \frac{e^{\theta_E/T}}{(e^{\theta_E/T} - 1)^2},$$

where $x = \hbar\omega/k_B T$, ω is the Debye frequency, θ_D and θ_E are the Debye and Einstein temperatures, respectively, and c_D and c_E are constants containing numbers of oscillators and

degrees of freedom. These four parameters are treated as fitting parameters, and the combined model adequately describes the experimental data over the entire temperature range (solid line in Figure 4). The Debye and Einstein temperatures obtained are $\theta_D \approx 167 \pm 3$ K and $\theta_E \approx 486 \pm 11$ K, respectively, with corresponding constants $c_D \approx 248 \pm 4$ J/mol·K and $c_E \approx 56 \pm 1$ J/mol·K. The Debye temperature is in good agreement with the value derived from the low temperature data. The two distinct temperatures, θ_D and θ_E , indicate the existence of two different vibrational modes in Ba₂TeO, consistent with the observation of two distinct structural moieties, BaTe and BaO. Since the BaO layer is under compression, it is expected to be stiff, thereby contributing to the heat capacity at higher temperatures, consistent with the higher Einstein temperature ascribed to this layer. The lower Debye temperature then corresponds to the BaTe layers and is consistent with the Debye temperature obtained from the low temperature data only.

3.5 Optical Absorbance

The absorbance spectrum spanning from the UV to NIR is displayed in Figure 5, for a single crystal where the electric field of the incident light was oriented in the plane of the sample, i.e., $E \perp c$ -axis. As the UV range is approached, a sharp onset in absorbance is observed, which is a clear manifestation of a band edge. A linear extrapolation of the absorbance near the band edge intercepts the x -axis at 2.93 eV, which is assigned as the band gap energy.

Figure 5: Absorbance as a function of energy from UV-VIS optical measurements. The electric field of the incident light was oriented in the plane of the sample ($E \perp c$ -axis). The band gap energy is 2.93 eV, obtained by linear extrapolation of the absorbance near the band edge to the x -axis. The inset shows the calculated absorption coefficient as a function of energy for the electric field in two directions: perpendicular and parallel to the c -axis.

By calculating the dielectric tensor, the optical properties for a material can be obtained. The total dielectric function $\varepsilon(\omega)$ is expressed as the sum of a real and an imaginary part, $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$, with the absorption coefficient α calculated using the relation $\alpha = 4\pi\kappa/\lambda$, where κ is the extinction coefficient, obtained from $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ [56]. Since Ba_2TeO crystallizes with tetragonal symmetry, it has only two nonzero second order dielectric tensor components, $\varepsilon^{xx}(\omega) = \varepsilon^{yy}(\omega)$ and $\varepsilon^{zz}(\omega)$. Therefore, calculations were performed for both an electric field perpendicular and parallel to the c -axis. As can be seen in the inset to Figure 5, the absorption coefficient is anisotropic. The calculated absorption edge is approximately 2.5 eV in both orientations; however, the band gap energy differs clearly between the two orientations. In the case of an electric field perpendicular to the c -axis, a linear extrapolation of α intercepts the x -axis at approximately 2.9 eV, in good agreement with the experimental absorbance measurements. In the case of an electric field parallel to the c -axis, a linear extrapolation yields a band gap energy of approximately 3.6 eV, i.e., a nearly 25 % increase of the gap energy when compared to the $E \perp c$ -axis case.

As grown crystals are not transparent, and thicker samples show optical absorption starting in the infrared region, extending to about 2.2 eV. This absorption is likely due to midgap states due to impurities, likely from the crucible. By exfoliating the samples, this defect absorption could be reduced, and thin samples were transparent to the eye.

4. Conclusion

A new layered oxytelluride, Ba_2TeO , has been synthesized in single crystalline form using a barium metal flux. Ba_2TeO is comprised of alternating inverse PbO-type BaO layers and slightly

puckered NaCl-type BaTe layers in a LuNiBC-related structure type. Heat capacity data show that the relaxed BaTe dominates the heat capacity at lower temperatures, with the compressed, stiff, BaO layer contributing to the heat capacity at high temperatures. Optical absorbance measurements revealed a band gap of 2.93 eV, a value that is corroborated by calculations of the absorption coefficient and density of states.

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References

- [1] H. Hiramatsu, H. Kamioka, K. Ueda, H. Ohta, T. Kamiya, M. Hirano, H. Hosono, *Physica Status Solidi (a)* 203 (2006) 2800-2811.
- [2] H. Hiramatsu, H. Yanagi, T. Kamiya, K. Ueda, M. Hirano, H. Hosono, *Chemistry of Materials* 20 (2008) 326-334.
- [3] D.C. Johnston, *Advances in Physics* 59 (2010) 803-1061.
- [4] C. Barreteau, L. Pan, E. Amzallag, L.D. Zhao, D. Bérardan, N. Dragoe, *Semiconductor Science and Technology* 29 (2014) 064001(10).
- [5] P. Vaqueiro, G. Guélou, M. Stec, E. Guilmeau, A.V. Powell, *Journal of Materials Chemistry A* 1 (2013) 520-523.
- [6] D. Zou, S. Xie, Y. Liu, J. Lin, J. Li, *Journal of Materials Chemistry A* 1 (2013) 8888-8896.
- [7] C. Barreteau, L. Pan, Y.-L. Pei, L.D. Zhao, D. Bérardan, N. Dragoe, *Functional Materials Letters* 6 (2013) 1370007(5).
- [8] H. Ohta, K. Nomura, H. Hiramatsu, K. Ueda, T. Kamiya, M. Hirano, H. Hosono, *Solid-State Electronics* 47 (2003) 2261-2267.
- [9] H. Hosono, *Thin Solid Films* 515 (2007) 6000-6014.
- [10] T. Kamiya, H. Hosono, *International Journal of Applied Ceramic Technology* 2 (2005) 285-294.

- [11] G.Q. Lin, H. Gong, P. Wu, *Physical Review B* 71 (2005) 085203(5).
- [12] K. Ueda, S. Inoue, S. Hirose, H. Kawazoe, H. Hosono, *Applied Physics Letters* 77 (2000) 2701-2703.
- [13] T. Kamiya, K. Ueda, H. Hiramatsu, H. Kamioka, H. Ohta, M. Hirano, H. Hosono, *Thin Solid Films* 486 (2005) 98-103.
- [14] K. Ueda, H. Hiramatsu, M. Hirano, T. Kamiya, H. Hosono, *Thin Solid Films* 496 (2006) 8-15.
- [15] S. Ramasubramanian, M. Rajagopalan, J. Kumar, R. Thangavel, *Journal of Applied Physics* 106 (2009) 023720(6).
- [16] A.P. Richard, J.A. Russell, A. Zakutayev, L.N. Zakharov, D.A. Keszler, J. Tate, *Journal of Solid State Chemistry* 187 (2012) 15-19.
- [17] Y. Ohki, K. Takase, Y. Takahashi, Y. Takano, K. Sekisawa, *Journal of Alloys and Compounds* 408-412 (2006) 98-100.
- [18] M.L. Liu, L.B. Wu, F.Q. Huang, L.D. Chen, J.A. Ibers, *Journal of Solid State Chemistry* 180 (2007) 62-69.
- [19] S.J. Clarke, P. Adamson, S.J.C. Herkelrath, O.J. Rutt, D.R. Parker, M.J. Pitcher, C.F. Smura, *Inorganic Chemistry* 47 (2008) 8473-8486.
- [20] H. Kamioka, H. Hiramatsu, M. Hirano, K. Ueda, T. Kamiya, H. Hosono, *Journal of Luminescence* 112 (2005) 66-70.
- [21] K. Ueda, H. Hosono, *Journal of Applied Physics* 91 (2002) 4768-4770.
- [22] H. Hiramatsu, K. Ueda, H. Ohta, M. Hirano, T. Kamiya, H. Hosono, *Applied Physics Letters* 82 (2003) 1048-1050.
- [23] G.W. Leddicotte, *The Radiochemistry of Tellurium*. Subcommittee on Radiochemistry, National Academy of Sciences-National Research Council, 1961.
- [24] N.N. Greenwood, A. Earnshaw, *Chemistry of the Elements*. 2nd ed.; Butterworth-Heinemann, Oxford, UK, 1997.
- [25] P. Villars, K. Cenzual, *Pearson's Crystal Data - Crystal Structure Database for Inorganic Compounds*. ASM International, Materials Park, Ohio, USA, 2012/13.
- [26] B. Gil, D.J. Dunstan, *Semiconductor Science and Technology* 6 (1991) 428-438.
- [27] A.M. Smith, S. Nie, *Accounts of Chemical Research* 43 (2010) 190-200.
- [28] R.E. Bailey, S. Nie, *Journal of the American Chemical Society* 125 (2003) 7100-7106.
- [29] A.J.K. Haneveld, F. Jellinek, *Journal of Inorganic & Nuclear Chemistry* 26 (1964) 1127-1128.
- [30] L. Shlyk, J. Stępień-Damm, R. Troć, *Journal of Crystal Growth* 154 (1995) 418-421.
- [31] E.W. Breeze, N.H. Brett, *Journal of Nuclear Materials* 40 (1971) 113-115.
- [32] H. Noël, M. Potel, L. Shlyk, D. Kaczorowski, R. Troć, *Journal of Alloys and Compounds* 217 (1995) 94-96.
- [33] D. Kaczorowski, R. Troć, L. Shlyk, H. Noël, A. Zaleski, *Journal of Magnetism and Magnetic Materials* 140-144 (1995) 1437-1438.
- [34] F.A. Weber, T. Schleid, *Zeitschrift für Anorganische und Allgemeine Chemie* 625 (1999) 1833-1838.
- [35] J. Llanos, S. Conejeros, R. Cortés, V. Sánchez, P. Barahona, O. Peña, *Materials Research Bulletin* 43 (2008) 312-319.
- [36] J.B. Whalen, T. Besara, R. Vasquez, E. Herrera, J. Sun, D. Ramirez, R.L. Stillwell, S.W. Tozer, T.D. Tokumoto, S.A. McGill, J. Allen, M. Davidson, T. Siegrist, *Journal of Solid State Chemistry* 203 (2013) 204-211.

- [37] Agilent Technologies, CrysAlisPro, Version 1.171.36.28. Agilent Technologies UK Ltd., Oxford, UK, 2012.
- [38] P.W. Betteridge, J.R. Carruthers, R.I. Cooper, K. Prout, D.J. Watkin, *Journal of Applied Crystallography* 36 (2003) 1487. CRYSTALS version 14.40b was used for the refinement.
- [39] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M.C. Burla, G. Polidori, M. Camalli, *Journal of Applied Crystallography* 27 (1994) 435.
- [40] G. Bergerhoff, I.D. Brown, in: F.H. Allen, G. Bergerhoff, R. Sievers, (Eds.), *Crystallographic Databases*, International Union of Crystallography, Chester, 1987, pp. 77-95.
- [41] P. Hohenberg, W. Kohn, *Physical Review* 136 (1964) B864-B871.
- [42] W. Kohn, L.J. Sham, *Physical Review* 140 (1965) A1133-A1138.
- [43] K. Schwarz, P. Blaha, G.K.H. Madsen, *Computer Physics Communications* 147 (2002) 71-76.
- [44] D. Singh, *Planewaves, Pseudopotentials and the LAPW Method*. Kluwer Academic, Boston, MA, 1994.
- [45] F. Tran, P. Blaha, *Physical Review Letters* 102 (2009) 226401(4).
- [46] L.-G. Liu, *Journal of Applied Physics* 42 (1971) 3702-3704.
- [47] J.F. Ackerman, *Journal of Solid State Chemistry* 92 (1991) 496-513.
- [48] Y. Doi, W. Nakamori, Y. Hinatsu, *Journal of Physics: Condensed Matter* 18 (2006) 333-344.
- [49] R.V. Shpanchenko, E.V. Antipov, L.M. Kovba, *Zhurnal Neorganicheskoi Khimii* 38 (1993) 599-605.
- [50] S.T. Weir, Y.K. Vohra, A.L. Ruoff, *Physical Review B* 33 (1986) 4221-4226.
- [51] V. Johnson, W. Jeitschko, *Journal of Solid State Chemistry* 11 (1974) 161-166.
- [52] T. Siegrist, H.W. Zandbergen, R.J. Cava, J.J. Krajewski, W.F. Peck Jr, *Nature* 367 (1994) 254-256.
- [53] E.P. Marusin, O.I. Bodak, A.O. Tsokol, M.G. Baivelman, *Kristallografiya* 30 (1985) 584-586.
- [54] C. Kittel, *Introduction to Solid State Physics*. 7th ed.; John Wiley & Sons, Inc., New York, 1996.
- [55] N.W. Ashcroft, N.D. Mermin, *Solid State Physics*. Saunders College, Philadelphia, 1976.
- [56] F. Wooten, *Optical Properties of Solids*. Academic Press, New York, 1972.