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ARTICLE

Synthesis and Structural Characterization of the layered Selenogallate $RbGaSe_2$

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Dedicated to Professor Wolfgang Schnick on the Occasion of his 60th Birthday

Abstract. The chalcogenogallate $RbGaSe_2$ was synthesized by thermal decomposition of rubidium azide in the presence of gallium selenide and selenium. $RbGaSe_2$ crystallizes in the monoclinic space group $C2/c$ (no. 15) with the lattice parameters a = 10.954(1) Å, b = 10.949(1) Å, c = 16.064(1) Å, β = 99.841(4)°, V = 1898.2(2) Å^3, and Z = 16 (single-crystal data, 20 °C) in the $TlGaSe_2$ structure type. Its crystal structure features anionic layers $^2_\infty[Ga_4Se_8{}^{4-}]$ with a van der Waals distance of 3.30(1) Å. Thermal analysis revealed a melting point of about 930 °C. Using UV/Vis diffuse reflectance spectroscopy, a wide bandgap of 3.16 eV was determined for the colorless semiconductor. The bonding situation in the compound was further compared with the isotypic cesium phases based on the results from Raman spectroscopy and DFT calculations. The slight shifts of the Raman bands suggest a slightly higher covalency of the rubidium compound.

Introduction

Due to their semiconducting properties, group 13 chalcogeno-metallates containing alkali metal cations $M_xT_yQ_z$ (M = alkali metal, T = triel, Q = chalcogen) are interesting materials for technical applications.[1] These chalcogenotrielates are known to crystallize in a large variety of diverse crystal structure types.[2] The smallest structural building unit of these structures are TQ_4 tetrahedra. Condensation of these building blocks yields more complex poylmeric one-, two- or three-dimensional anions, which are embedded in a cationic surrounding of the akali metal cations. The MTQ_2 phases are known for almost all possible element combinations among these chalcogenotrielates. The dominating structure type among these solids is the $TlGaSe_2$ structure type,[3] featuring anionic layers $^2_\infty[T_4Q_8{}^{4-}]$, which seems to have a very high tolerance for different combinations of the elements involved.[4] Another possible anionic substructure of these MTQ_2 phases are anionic chains $^1_\infty[TQ_2{}^{-}]$ as found in the Tl_2Se_2[5] and $KFeS_2$ structure types.[6]

In this paper, we report on the synthesis and structural characterization of $RbGaSe_2$, one of the very few missing phases MTQ_2 in the ternary systems of alkali metal, triel, and chalcogen. The title compound was further characterized by Raman- and UV/Vis spectroscopy. We examined the solid at high temperatures regarding a possible phase-transition similar to the isotypic cesium compounds $CsGaQ_2$-$mC64$ (Q = S, Se).[7] This is especially interesting in order to further investigate the chemical similarities of Rb with Cs and K.

Results and Discussion

Crystal Structure Determination of $RbGaSe_2$

$RbGaSe_2$ forms air- and moisture sensitive, colorless, plate-shaped crystals. In order to minimize the significant stacking disorder present in this compound and isotypic phases,[8] a small rod-like fragment was broken off from a suitable plate-shaped crystal. The crystal structure was solved from single-crystal X-ray diffraction data collected at 20 °C. Due to the high fluorescence of the rubidium and selenium atoms when using Mo-K_α radiation, Cu-K_α radiation was used for the measurement. The compound crystallizes in the monoclinic space group $C2/c$ (no. 15) with the lattice parameters a = 10.954(1) Å, b = 10.949(1) Å, c = 16.064(1) Å, β = 99.841(4)°, V = 1898.2(2) Å^3, and Z = 16 (single-crystal data, 20 °C). The crystal structure was solved by charge flipping methods using SUPERFLIP,[9] implemented in Jana 2006,[10] and refined to R_1 = 0.0404 and wR_2 = 0.0863 (all data) using Jana2006.[10] Similar to the isotypic compound $CsGaSe_2$-$mC64$, $RbGaSe_2$ single crystals are notoriously twinned. Using TwinRotMat of the PLATON software package,[11] a twin matrix identical to $CsGaSe_2$-$mC64$ was found.[7a] Details on the structure solution and refinement are listed in Table 1. The atomic coordinates, displacement parameters as well as selected interatomic distances and angles are provided in the supplementary material (Tables S1–S3, Supporting Information).

$RbGaSe_2$ crystallizes isotypic to $CsGaSe_2$-$mC64$ and many related compounds MTQ_2 (M = Na, K, Rb, Cs, Tl; T = Al, Ga, In; Q = S, Se, Te) in the $TlGaSe_2$ structure type.[3] The anisotropic crystal structure of this solid features anionic layers $^2_\infty[Ga_4Se_8{}^{4-}]$, composed of corner sharing Ga_4Se_{10} super-tetra-

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Table 1. Crystallographic data for $RbGaSe_2$.

	$RbGaSe_2$
Formula weight M /g·mol^{-1}	313.11
Color and shape	Colorless rod-like fragment
Crystal size /mm^3	$0.24 \times 0.04 \times 0.02$
Space group	$C2/c$ (no. 15)
Crystal system	monoclinic
Lattice parameters from single crystal	
a /Å	10.954(1)
b /Å	10.949(1)
c /Å	16.064(1)
β /°	99.841(4)
Unit cell volume V /Å^3	1898.2(2)
Number of formula units Z	16
Calculated density ρ /g·cm^{-3}	4.382
Diffractometer	Rigaku Supernova
Temperature T /°C	20(1)
Wavelength λ /Å	1.54184
Absorption coeff. μ(Cu-K_α) /mm^{-1}	36.236
θ range /°	5.59–76.52
Index range	$-13 \le h \le 12$ $-13 \le k \le 13$ $-20 \le l \le 20$
No. of reflections collected	11049
Independent reflections	2045
R_{int}, R_σ	0.0119, 0.0375
Completeness to θ = 76.52°	99.9 %
Absorption correction	Numerical, CrysAlisPro [12]
Structure solution	Charge flipping, Superflip [9]
Structure refinement	Jana2006 [10]
Twin law	–1 0 0, 0 –1 0, ½ 0 1
Twin fraction	26.1(4) %
Data / restraints / parameters	2045 / 0 / 76
GooF, F(000)	1.70, 2176
R_1, wR_2 [$I > 3\sigma(I)$]	0.0298, 0.0737
R_1, wR_2 [all data]	0.0404, 0.0863
Extinction coefficient G_{iso}	0.144(1)
Largest diff. peak and hole /e·Å^{-3}	1.26, –1.32

hedra (Figure 1). These layers are stacked along [001] and are separated by Rb atoms. The van der Waals distance between two adjacent layers is 3.30(1) Å. Both independent Ga^{3+} sites are tetrahedrally coordinated by Se^{2-} anions. The interatomic distances in these slightly distorted tetrahedra range from d(Ga–Se) = 2.388(1) Å to d(Ga–Se) = 2.428(1) Å. The angles Se–Ga–Se range from 106.04(3)° to 113.45(3)°. These values differ only slightly from the sum of the ionic radii,[13] $d(Ga^{3+}–Se^{2-}) \approx 2.5$ Å, and are in good agreement with comparable compounds like $Cs_2Ga_2Se_5$,[14] and both polymorphs of $CsGaSe_2$[7a] (Q = S, Se). The two independent Rb^+ sites are 6+2 fold coordinated by Se^{2-}, resulting in bicapped trigonal prisms (Figure 1). The interatomic distances in these prisms range from d(Rb–Se) = 3.428(1) Å to d(Rb–Se) = 3.555(1) Å while the distances to the capping atoms ranging from d(Rb–Se) = 3.896(1) Å to d(Rb–Se) = 3.911(1) Å are significantly longer. The $RbSe_8$ prisms are connected by common edges, faces, and the capping atoms (Se1, Se2). The eightfold interconnected rubidium atoms form an irregular topological network. The distances between the rubidium atoms in one layer are d(Rb–Rb) < 5 Å, whereas the distances between adjacent layers are in the range of 5.4 Å < d(Rb–Rb) < 5.5 Å.

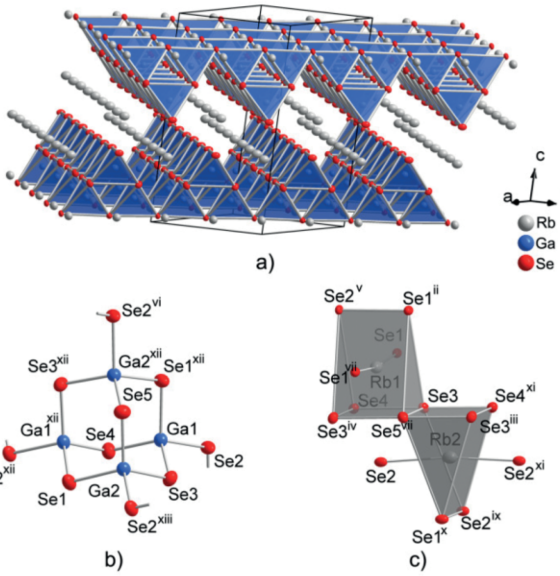

Figure 1. The crystal structure of $RbGaSe_2$, showing: (a) stacking of the anionic selenogallate layers; (b) a supertetrahedral Ga_4Se_{10} unit; (c) coordination polyhedra of the Rb atoms.

Thermal Analysis

In order to analyze the behavior of $RbGaSe_2$ at high temperature, the solid was investigated by high-temperature X-ray powder diffraction in the temperature range from 20–900 °C. The measurement revealed no phase-transitions for $RbGaSe_2$ contrary to the isotypic phases $CsGaQ_2$-$mC64$ (Q = S, Se)[7] as shown in Figure S1 (Supporting Information). As no melting point of the sample could be observed in the temperature region investigated by diffraction experiments, we performed a differential thermal analysis (DTA) up to 1000 °C. This measurement revealed a melting point of about 930 °C (Figure S2, Supporting Information).

Raman Spectroscopy

The Raman spectrum of $RbGaSe_2$ is shown in Figure 2. The bands at 281, 262, and 235 cm^{-1} result from Ga–Se stretching modes, whereas the vibrations at 215, 196, and 135 cm^{-1} can be attributed to Ga–Se deformation modes.[7a,14–15] All vi-

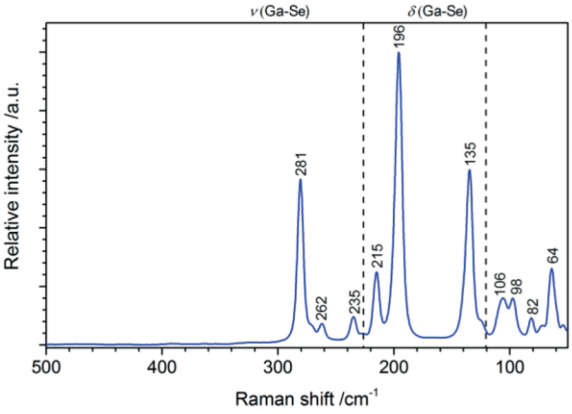

Figure 2. Raman spectrum of $RbGaSe_2$.

brations at lower frequencies are tentatively assigned to lattice vibrations. The Raman spectra of $RbGaSe_2$ and $CsGaSe_2$-*mC*64[7a] are almost identical. The vibration frequencies in the rubidium compound, however, show a small blue-shift of about 2–10 cm^{-1} which indicates stronger Ga–Se bonding interactions in $RbGaSe_2$ compared to $CsGaSe_2$-*mC*64.

Optical Properties

The optical bandgap of $RbGaSe_2$ was determined by using UV/Vis diffuse reflectance spectroscopy (Figure 3). The absorption spectrum was calculated using a modified Kubelka-Munk function.[16] Extrapolation of the linear part onto the baseline revealed a wide bandgap of 3.16 eV which is in good agreement with the colorless powdered substance.

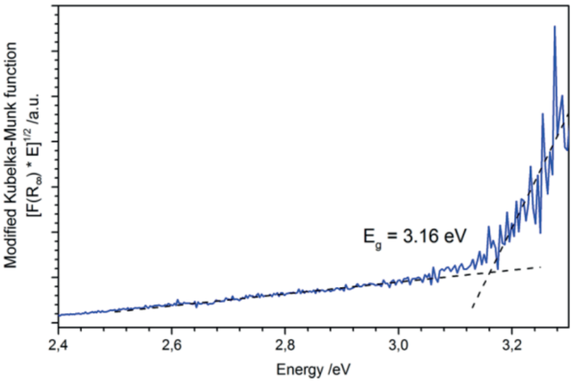

Figure 3. Diffuse reflectance spectrum of $RbGaSe_2$. The optical bandgap was determined by extrapolation of the linear part of the modified Kubelka-Munk function onto the baseline, which is indicated by the dashed lines.

We further attempted to calculate the electronic band structure of $RbGaSe_2$ from relativistic DFT calculations. Similar to $CsGaSe_2$-*mC*64,[7a] we observed significant discrepancies between the experimental and calculated bandgaps using the GGA[17] and LSDA[18] functionals. The most plausible result is depicted in Figure 4. Interestingly, the bandgap values are identical for $CsGaSe_2$-*mC*64 ($E_g^{exp} = 3.16$ eV, $E_g^{calc} \approx 2.0$ eV) and $RbGaSe_2$ ($E_g^{exp} = 3.16$ eV, $E_g^{calc} \approx 2.0$ eV). Furthermore, the electronic structures of both compounds are basically identical except for the alkali metal states, which of course do not contribute to the bandgap energy. The highest occupied bands are mainly due to Se-4p states, whereas the lowest energies of the conduction band show contributions mostly from Ga-4s states. This observation further confirms our previous assumption that the electronic properties of these compounds strongly depend on the covalent interactions between gallium and chalcogen atoms, whereas the alkali metals do not significantly contribute to the bandgap.[7,19–20] The fact that the DFT calculations for the selenides show these discrepancies, which were not observed in case of the sulfides,[7b] indicates that conventional calculations significantly underestimate the Ga–Se interactions in the selenogallate layers.

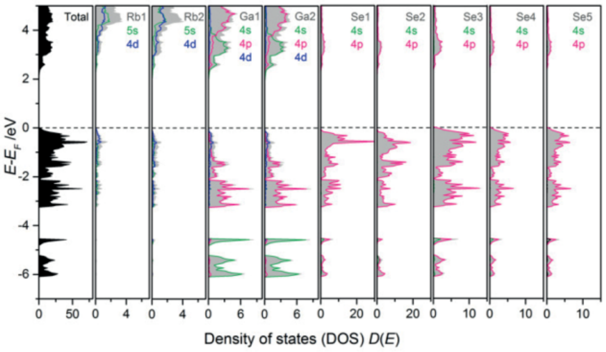

Figure 4. Calculated total (TDOS) and partial density of states (PDOS) for $RbGaSe_2$. The highest occupied bands are mainly due to Se-4p states whereas the lowest energies of the conduction band show contributions mostly from Ga-4s states.

Conclusions

$RbGaSe_2$, a new phase in the ternary systems of alkali metal, gallium, and selenium was synthesized and structurally characterized. Contrary to the isotypic cesium phases, $RbGaSe_2$ does not undergo a polymorphic phase-transition at elevated temperatures below its melting point. DFT calculations combined with Raman spectroscopy revealed that even though the electronic structure of $RbGaSe_2$ and $CsGaSe_2$-*mC*64 are almost identical, slightly stronger covalent Ga–Se interactions can be observed in the rubidium compound.

Experimental Section

Synthesis of the Starting Materials: GaSe was prepared by chemical vapor transport reaction from gallium (Chempur 99.99 %) and selenium (Chempur 99.999 %) using iodine (Sigma-Aldrich 99.8 %) as transporting agent.[21] Pure RbN_3 was obtained by passing hydrazoic acid (prepared by acidifying an aqueous solution of NaN_3 (Sigma-Aldrich 99.0 %) into an aqueous solution of Rb_2CO_3 (Sigma-Aldrich 99 %).[22]

Caution: Condensed HN_3 is highly explosive. Tools made from transition metals must be avoided.

Synthesis of $RbGaSe_2$: The title compound was synthesized by controlled thermal decomposition (0.2 g batch size, heating rate 0.5 $K\cdot min^{-1}$) of RbN_3 combined with a stoichiometric mixture of GaSe and selenium in a quartz glass ampoule under dynamic vacuum conditions. Upon heating, the azide decomposes to the pure alkali metal which immediately reacts with the other starting materials, resulting in an inhomogeneous raw product. A flame sealed ampoule containing this raw product was annealed at 850 °C to yield pure $RbGaSe_2$. The advantage of this azide route is the avoidance of handling larger amounts of pure and highly reactive alkali metals, which are difficult to dose in proper portions. However, since the azide decomposes to the elements, the reaction can be regarded as equivalent to a batch containing only the elements.

Single-Crystal X-ray Diffraction: Data collections on suitable single-crystals were performed with a Rigaku Supernova at 20 °C using monochromatized Cu-K_α radiation ($\lambda = 1.54184$ Å). The diffraction data were corrected for Lorentz- and polarization effects and corrected by a numerical absorption correction using the CrysAlisPro software package.[12] The resulting data set had a completeness of 99.9 % within 75° θ. The crystal structure was solved by charge flipping methods using SUPERFLIP[9] (implemented in Jana2006[10]) and refined on F^2

with Jana2006[10] using full-matrix least-squares methods. The experimental parameters and details on the structure solution and refinement are summarized in Table 1.

Further details of the crystal structures investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: +49-7247-808-666; E-Mail: crysdata@fiz-karlsruhe.de, http://www.fiz-karlsruhe.de/request for deposited data.html) on quoting the depository numbers CSD-433600.

X-ray Powder Diffraction: The X-ray powder diffraction experiments were performed with a STOE STADI P diffractometer equipped with a Dectris Mythen 1 K detector and a high-temperature capillary furnace. Monochromatized Mo-$K_{\alpha1}$ radiation (λ = 0.70930 Å) was used in all experiments. The air sensitive samples were flame sealed in a 0.3 mm quartz glass capillary and placed in another 0.5 mm quartz glass capillary because of the furnace architecture. The WinX^{POW} software package from STOE & Cie was used for data collection and processing.[23] The furnace temperature was controlled by a Eurotherm 24.16 controller (ΔT = ±1 °C). A comparison of the diffraction patterns of phase-pure $RbGaSe_2$, measured with Cu-$K_{\alpha1}$ radiation (λ = 1.540598 Å), with a calculated pattern based on the single crystal data is shown in Figure S3 (Supporting Information).

Differential Thermal Analysis: Differential thermal analysis of the compound was performed with a SETARAM TG-DTA 92 16.18 in an evacuated quartz glass ampoule using Al_2O_3 as reference material. The measurements were performed in the range of 25–1000 °C with a heating- and cooling rate of 10 K·min^{-1} (2 cycles).

Vibrational Spectroscopy: The Raman spectrum was recorded with a DXR^{TM} SmartRaman Spectrometer from Thermoscientific (excitation wavelength λ = 532 nm) in the range of 50–1000 cm^{-1} with a resolution of 0.5 cm^{-1}.

UV/Vis Spectroscopy: Diffuse reflectance measurements were performed with a Bruins Omega 20 UV/Vis spectrometer using $BaSO_4$ as a reference (100 % reflectance). The absorption spectrum was calculated using a modified Kubelka-Munk function.[16]

DFT Calculations: The first-principles calculations were carried out within the framework of density functional theory (DFT) with exchange-correlation functionals in the generalized gradient approximation (GGA) according to Perdew-Burke-Enzerhof (PBE),[17] and the local-spin-density approximation (LSDA).[18] The full potential local orbital code FPLO14[24] with a k-grid mesh of $12 \times 12 \times 12$ was applied for total energy and band structure calculations based on the experimentally obtained structures. All of these calculations converged with a maximum divergence of $<10^{-7}$ Hartree.

Supporting Information (see footnote on the first page of this article): Tables S1-S3 display atomic coordinates, anisotropic displacement parameters, and selected interatomic distances of $RbGaSe_2$. Figures S1-S3 show the evolution of the X-ray powder diffractogram in the range 20-900 °C, a DTA curve from 25 to 1000 °C, and an experimental X-ray powder diffractogram in comparison to a calculated one.

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Keywords: Crystal structure; Density functional calculations; Layered material; Selenogallate; Semiconductors

References

[1] a) J.-J. Zondy, F. Bielsa, A. Douillet, L. Hilico, O. Acef, V. Petrov, A. Yelisseyev, L. Isaenko, P. Krinitsin, *Opt. Lett.* **2007**, *32*, 1722–1724; b) V. Petrov, A. Yelisseyev, L. Isaenko, S. Lobanov, A. Titov, J.-J. Zondy, *Appl. Phys. B: Laser Opt.* **2004**, *78*, 543–546.
[2] B. Krebs, *Angew. Chem.* **1983**, *95*, 113–134.
[3] D. Müller, F. E. Poltmann, H. Hahn, *Z. Naturforsch.* **1974**, *29b*, 117–118.
[4] a) M. D. Ward, E. A. Pozzi, R. P. Van Duyne, J. A. Ibers, *J. Solid State Chem.* **2014**, *212*, 191–196; b) F. Q. Huang, B. Deng, D. E. Ellis, J. A. Ibers, *J. Solid State Chem.* **2005**, *178*, 2128–2132; c) S. J. Ewing, D. I. Woodward, A. V. Powell, P. Vaqueiro, *J. Solid State Chem.* **2013**, *204*, 159–165; d) B. Eisenmann, A. Hofmann, *Z. Kristallogr.* **1991**, *197*, 171–172; J. Kim, T. Hughbanks, *J. Solid State Chem.* **2000**, *149*, 242–251; e) P. Lemoine, D. Carre, M. Guittard, *Acta Crystallogr., Sect. C* **1984**, *40*, 910–912; f) K. Feng, D. Mei, L. Bai, Z. Lin, J. Yao, Y. Wu, *Solid State Sci.* **2012**, *14*, 1152–1156; B. Eisenmann, A. Hofmann, *Z. Kristallogr.* **1991**, *195*, 318; g) P. Wang, X.-Y. Huang, Y.-L. Liu, J. Li, H.-Y. Guo, *Huaxue Xuebao* **2000**, *58*, 1005–1008; h) A. Kumari, K. Vidyasagar, *Acta Crystallogr., Sect. E* **2005**, *61*, i193-i195; i) E. J. Wu, M. A. Pell, T. M. Fuelberth, J. A. Ibers, *Z. Kristallogr.* **1997**, *212*, 91; j) H.-Y. Zeng, F.-K. Zheng, R.-P. Chen, Z.-C. Dong, G.-C. Guo, J.-S. Huang, *J. Alloys Compd.* **2007**, *432*, 69–73; k) H. Lin, J.-N. Shen, L. Chen, L.-M. Wu, *Inorg. Chem.* **2013**, *52*, 10726–10728.
[5] J. A. A. Ketelaar, W. H. t'Hart, M. Moerel, D. Polder, *Z. Kristallogr.* **1939**, *101*, 396–405.
[6] J. W. Boon, C. H. Mac Gillavry, *Recueil Trav. Chim. Pays-Bas* **1942**, *61*, 910–920.
[7] a) D. Friedrich, M. Schlosser, A. Pfitzner, *Cryst. Growth Des.* **2016**, *16*, 3983–3992; b) D. Friedrich, M. Schlosser, R. Weihrich, A. Pfitzner, *Inorg. Chem. Frontiers* **2017**, *4*, 393–400.
[8] L. Kienle, V. Duppel, A. Simon, M. Schlosser, O. Jarchow, *J. Solid State Chem.* **2004**, *177*, 6–16.
[9] L. Palatinus, G. Chapuis, *J. Appl. Crystallogr.* **2007**, *40*, 786–790.
[10] V. Petříček, M. Dušek, L. Palatinus, *Z. Kristallogr., Crystalline Mater.* **2014**, *229*, 345.
[11] A. Spek, *J. Appl. Crystallogr.* **2003**, *36*, 7–13.
[12] Rigaku Oxford Diffraction, CrysAlisPro, Version 1.171.38.43, **2015**.
[13] R. D. Shannon, *Acta Crystallogr., Sect. A* **1976**, *32*, 751–767.
[14] D. Friedrich, M. Schlosser, A. Pfitzner, *Z. Anorg. Allg. Chem.* **2014**, *640*, 826–829.
[15] J. Do, M. G. Kanatzidis, *Z. Anorg. Allg. Chem.* **2003**, *629*, 621–624.
[16] a) H. Kisch, *Angew. Chem. Int. Ed.* **2013**, *52*, 812–847; b) P. Kubelka, F. Munk, *Z. Technol. Phys.* **1931**, 593.
[17] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.
[18] J. W. Negele, *Phys. Rev. C* **1970**, *1*, 1260–1321.
[19] D. Friedrich, F. Pielnhofer, M. Schlosser, R. Weihrich, A. Pfitzner, *Chem. Eur. J.* **2015**, *21*, 1811–1817.
[20] D. Friedrich, M. Schlosser, A. Pfitzner, *Cryst. Growth Des.* **2017**, *17(9)*, 4887-4892.
[21] T. Ishii, N. Kambe, *J. Cryst. Growth* **1986**, *76*, 489–493.
[22] R. Suhrmann, K. Clusius, *Z. Anorg. Allg. Chem.* **1926**, *152*, 52–58.
[23] Stoe & Cie GmbH, *WinX^{POW}*, Version 3.10, Darmstadt, Germany, **2017**.
[24] K. Koepernik, H. Eschrig, *Phys. Rev. B* **1999**, *59*, 1743–1757.

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