# Orthorhombic HP-PrO<sub>2</sub> – High-Pressure Synthesis and Crystal Structure

Almut Haberer<sup>[a]</sup> and Hubert Huppertz<sup>\*[a]</sup>

Dedicated to Professor Hans-Jörg Deiseroth on the Occasion of His 65th Birthday

Keywords: Praseodymium oxide; High-pressure; Solid-state structures; Rare Earths; Synthetic methods

**Abstract.** The high-pressure phase of  $PrO_2$  was synthesized under conditions of 5.5 GPa and 1000 °C in a Walker-type multianvil apparatus. The crystal structure was determined on the basis of single-crystal X-ray diffraction data collected at room temperature. The title compound

#### Introduction

The field of lanthanide dioxides  $LnO_2$  with a cubic fluorite structure was extensively studied in the past. Among these components, which are potentially applicable as laser hosts and optical component materials, CeO<sub>2</sub> has a wide range of applications in the industry under the name of Ceria. Being of great interest for the catalytic industry, it is widely used as oxygen storage in automobile exhaust catalysts [1–3]. PrO<sub>2</sub> is an insulator isostructural with UO<sub>2</sub> and NpO<sub>2</sub> at room temperature and exhibits antiferromagnetic ordering below  $T_{\rm N} = 13.5$  K. It can be synthesized in high purity by electrocrystallization [4]. PrO<sub>2</sub> was found to have an anomalously small-ordered moment in the antiferromagnetic phase [5]. Further studies revealed a cooperative Jahn–Teller distortion at  $T_{\rm D} = 120 \pm 2$  K and a related distortion of the antiferromagnetic structure below  $T_{\rm N}$  [6]. In order to determine the electronic ground state of PrO<sub>2</sub>, many studies were performed, including core-level photoabsorption, photoemission spectra, and neutron scattering [7, 8]. The publication of an influential model [9], which describes an intermediate valence state in the anomalous cuprate  $PrBa_2Cu_3O_{6+x}$  (PrBCO) similar to that proposed for the lanthanide dioxides, has increased interest in PrO2, making it a key reference compound in high-energy spectroscopic studies of PrBCO and related materials.

Several studies were performed on the high-pressure modifications of CeO<sub>2</sub> and PrO<sub>2</sub> in the past years. Crystallizing into the cubic fluorite structure under ambient pressure conditions, a transition of these compounds into the orthorhombic  $\alpha$ -PbCl<sub>2</sub>-type (cotunite) structure under pressure was reported.

In the case of CeO<sub>2</sub>, many high-pressure studies were performed and a crystal structure, obtained from *in situ* X-ray

E-Mail: Hubert.Huppertz@uibk.ac.at

crystallizes in the orthorhombic  $\alpha$ -PbCl<sub>2</sub>-type structure with the lattice parameters a = 637.6(3) pm, b = 384.4(2) pm, and c = 703.1(3) pm. The praseodymium ion is ninefold coordinated, the oxygen ions show either tetrahedral or square-pyramidal coordination spheres.

powder diffraction data by *Dyclos* et al. is found in the database [10]. The phase transition in CeO<sub>2</sub> occurs around 31 GPa [11] and bulk moduli of  $230 \pm 10$  GPa [10] and 220(9) GPa [12] were measured. The computational value of 357 GPa obtained by *Hill* et al., was significantly larger [13], whereas a study of *Gerward* et al. led to a lower calculated zero-pressure bulk modulus of 176.9 GPa [12]. Several computational studies concerning electronic, optical, and bonding properties were carried out [14–16]. The oxygen storage and surface properties were studied by *Skorodumova* et al. [17, 18], additionally the potential of CeO<sub>2</sub> as an UV absorber was investigated [19].

On PrO<sub>2</sub>, very few high-pressure studies were performed. Whereas the transformation into the orthorhombic high-pressure phase was measured *in situ* in a diamond-anvil cell with laser heating [20, 21], no single-crystal measurements and crystal structure parameters were reported so far. In high-pressure experiments by *Liu*, the fluorite structure of PrO<sub>2</sub> was stable up to 20 GPa; a phase transition into a possible  $\delta$ -Ni<sub>2</sub>Si type was postulated [20]. A zero-pressure bulk modulus of 187.8 GPa for PrO<sub>2</sub> was investigated [12]; its computational values are 250 GPa and 176.8 GPa [22].

This work presents a synthesis, by which single-crystals of the high-pressure phase HP-PrO<sub>2</sub> were yielded for the first time. A detailed description of the crystal structure, obtained from single-crystal X-ray diffraction measurements, is given.

### **Experimental Section**

Single-crystals of orthorhombic HP-PrO<sub>2</sub> were obtained as a by-product during a synthesis in the study of high-pressure rare-earth fluoride borates.  $Pr_6O_{11}$  (Strem Chemicals, 99.9 %),  $B_2O_3$  (Strem Chemicals, 99.9+%), and PrF<sub>3</sub> (Strem Chemicals, 99.9 %) were mixed at a molar ratio of 1:2:1 and filled into a boron nitride crucible (Henze BNP GmbH, HeBoSint<sup>®</sup> S10, Kempten, Germany). This crucible was placed into the center of an 18/11-assembly, which was compressed by eight tungsten carbide cubes (TSM-20 Ceratizit, Reutte, Austria). The details of preparing the assembly can be found in ref. [23–27].



<sup>\*</sup> Prof. Dr. H. Huppertz

 <sup>[</sup>a] Institut für Allgemeine, Anorganische und Theoretische Chemie Leopold-Franzens-Universität Innsbruck Innrain 52a
6020 Innsbruck, Austria

# ARTICLE

Pressure was applied by a multianvil device, based on a Walker-type module, and a 1000-ton press (both devices from the company Voggenreiter, Mainleus, Germany). The sample was compressed up to 5.5 GPa for 2.5 h, afterwards heated to 1000 °C in 15 min and kept there for 20 min. Afterwards, the sample was cooled down to 600 °C in 20 min, followed by quenching to room temperature after switching off heating. Decompression required 7.5 h. The recovered experimental MgOoctahedron (pressure transmitting medium, Ceramic Substrates & Components Ltd., Newport, Isle of Wight, UK) was broken apart and the sample carefully separated from the surrounding boron nitride crucible, obtaining dark brown irregularly-shaped crystals of HP-PrO<sub>2</sub>.

An experiment with pure  $Pr_6O_{11}$  under the conditions mentioned above did not produce the orthorhombic HP-PrO<sub>2</sub> phase.

**Crystal-Structure Analysis:** The sample was characterized by powder X-ray diffraction, which was performed in transmission geometry on a flat sample of the reaction product with a STOE STADI P powder diffractometer with Mo- $K_{\alpha 1}$  radiation (Ge monochromator,  $\lambda = 71.073$  pm). Reflections of orthorhombic HP-PrO<sub>2</sub> were identified, which tally well with the theoretical pattern simulated from single-crystal data. Additional reflections in the powder pattern of the sample show the presence of other yet unknown products. Because of this, a robust refinement with TOPAS was performed on the sample (Figure 1) [28]. The refined cell parameters for HP-PrO<sub>2</sub> from powder data

resulted in a = 638.52(2) pm, b = 384.48(2) pm, and c = 702.70(2) pm, with a volume of 172.52(1) Å<sup>3</sup>. This confirms the lattice parameters obtained from single-crystal X-ray diffraction (Table 1). The atomic position parameters were refined as well; they are in agreement with the parameters listed in Table 2. The whole robust refinement included 35 parameters.

Intensity data of a single-crystal of HP-PrO<sub>2</sub> were collected at room temperature with a Kappa CCD diffractometer (Bruker AXS/Nonius, Karlsruhe), equipped with a Miracol Fiber Optics Collimator and a Nonius FR590 generator (graphite-monochromatized Mo- $K_{a1}$  radiation,  $\lambda = 71.073$  pm). An absorption correction, based on multi-scans [29], was applied to the data set. All relevant details of the data collection and evaluation are listed in Table 1.

The structure solution and the parameter refinement (full-matrix leastsquares against  $F^2$ ) were successfully performed, using the SHELX-97 software suite [30, 31] with anisotropic atomic displacement parameters for all atoms. According to the systematic extinctions, the orthorhombic space groups *Pnma* and *Pn*2<sub>1</sub>*a* were derived. The structure solution was successfully performed in *Pnma* (no. 62). The final difference Fourier syntheses did not reveal any significant residual peaks in all refinements. The positional parameters of the refinements, anisotropic displacement parameters, interatomic distances, and interatomic angles are listed in the Table 2, 3, 4. Further information of the crystal

<b>Tuble 1.</b> Crystal data and structure refinement of the rice	Table 1.	Crystal	data	and	structure	refinement	of HP-PrC	)2.
---	----------	---------	------	-----	-----------	------------	-----------	-----

5	2	
Empirical Formula	PrO <sub>2</sub>	
Molar mass /g·mol <sup>-1</sup>	172.91	
Crystal system	orthorhombic	
Space group	<i>Pnma</i> (No. 62)	
Lattice parameters from powder data		
Powder diffractometer	Stoe Stadi P	
Radiation	Mo- $K_{\alpha 1}$ ( $\lambda = 71.073 \text{ pm}$ )	
a /pm	638.52(2)	
<i>b</i> /pm	384.48(2)	
c /pm	702.70(2)	
Volume /Å <sup>3</sup>	172.52(1)	
Single-crystal data		
Single-crystal diffractometer	Bruker AXS/Nonius Kappa CCD	
Radiation	Mo- $K_{a1}$ ( $\lambda = 71.073 \text{ pm}$ )	
a /pm	637.1(2)	
b /pm	383.90(8)	
c /pm	702.6(2)	
Volume /Å <sup>3</sup>	171.84(6)	
Formula units per cell	4	
Temperature /K	293(2)	
Calculated density /g·cm <sup>-3</sup>	6.684	
Crystal size /mm	$0.04 \times 0.03 \times 0.02$	
Absorption coefficient /mm <sup>-1</sup>	27.85	
F(000)	300	
$\theta$ range /deg	$4.3 \le \theta \le 32.4$	
Range in h k l	$\pm 9, \pm 5, \pm 10$	
Total no. reflections	2222	
Independent reflections	$349 \ (R_{\rm int} = 0.0304)$	
Reflections with $I > 2\sigma(I)$	341 ( $R_{\sigma} = 0.0181$ )	
Data/parameters	349/20	
Absorption correction	Multi-scan [29]	
Goodness-of-fit $[F^2]$	1.137	
Final R indices $[I > 2\sigma(I))$	$R_1 = 0.0144, wR_2 = 0.0380$	
R indices (all data)	$R_1 = 0.0150, wR_2 = 0.0384$	
Largest differ, peak, deepest hole $/e \cdot Å^{-3}$	1.33/-1.18	





**Figure 1.** Robust refinement of the experimental powder pattern (top) of the reaction sample, identifying orthorhombic HP-PrO<sub>2</sub> (top) as a product. The resulting difference curve (bottom) shows the reflection profile of the yet unidentified side products.

**Table 2.** Atomic coordinates and isotropic equivalent displacement parameters  $(U_{eq} / \text{Å}^2)$  for HP-PrO<sub>2</sub> (space group: *Pnma*).  $U_{eq}$  is defined as one-third of the trace of the orthogonalized  $U_{ii}$  tensor.

Atom	Wyckoff site	x	у	Ζ	$U_{\rm eq}$
Pr	4 <i>c</i>	0.27334(4)	1/4	0.39881(4)	0.0091(2)
O1	4 <i>c</i>	0.1462(6)	1/4	0.0799(5)	0.0103(6)
02	4 <i>c</i>	0.0240(5)	1/4	0.6651(5)	0.0115(6)

structure is available from the Fachinformationszentrum Karlsruhe (E-Mail: crysdata@fiz-karlsruhe.de), 76344 Eggenstein-Leopoldshafen, Germany, by quoting the Registry No. CSD-380398.

**Table 3.** Anisotropic displacement parameters  $(U_{ij} / Å^2)$  for HP-PrO<sub>2</sub> (space group: *Pnma*).

Atom	$U_{11}$	U <sub>22</sub>	$U_{33}$
Pr	0.0092(2)	0.0085(2)	0.0098(2)
01	0.010(2)	0.010(2)	0.012(2)
02	0.012(2)	0.015(2)	0.008(2)
	U <sub>12</sub>	U <sub>13</sub>	U <sub>23</sub>
Pr	0	-0.00078(8)	0
01	0	-0.002(2)	0
O2	0	0.005(2)	0

## **Results and Discussion**

Several studies were performed on the high-pressure modifications of CeO<sub>2</sub> and PrO<sub>2</sub> in the past years. Whereas these compounds crystallize in the cubic fluorite structure under ambient pressure conditions, a transition into the orthorhombic  $\alpha$ -PbCl<sub>2</sub>-type structure was reported under high-pressure conditions. It was also postulated that large metal-ion dioxides like CeO<sub>2</sub> and PrO<sub>2</sub> might be transformed into a  $\delta$ -Ni<sub>2</sub>Si-type struc-

**Table 4.** Interatomic distances /pm and angles /deg in HP-PrO<sub>2</sub>, calculated with the single-crystal lattice parameters.

Interatomic dist	tances /pm	
Pr–O1a (2 ×) 235.9(2)	Pr–O1b 238.0(4)	Pr-O1c 238.3(3)
Pr–O2a 245.4(3)	Pr–O2b (2 ×) 273.4(3)	Pr–O2c (2 ×) 283.7(3)
Interatomic ang	les /deg	
Pr-O1-Pr (2 ×) Pr-O1-Pr Pr-O1-Pr (2 ×) Pr-O1-Pr Pr-O1-Pr (2 ×)	$\begin{array}{c} 104.5(2) \\ 106.3(2) \\ 108.86(9) \\ 108.9(2) \\ 115.67(9) \end{array}$	Pr-O2-Pr     85.2(2) $Pr-O2-Pr$ (2) $Pr-P2-Pr$ (2) $Pr-P2-P2-Pr$ (2) $Pr-P2-P2-P2-P2-P2-P2-P2-P2-P2-P2-P2-P2-P2-$
	$\omega = 109.2$	$\emptyset = 106.6$

ture at high pressures [20]. According to *Jeitschko*, axial ratios can be used to distinguish between these very similar structure types, which differ only slightly in their atomic parameters [32]. For HP-CeO<sub>2</sub>, the axial ratio led to a classification as an  $\alpha$ -PbCl<sub>2</sub>-type structure [10].

Single-crystal data for HP-PrO<sub>2</sub> were now obtained for the first time, leading to lattice parameters of a = 637.1(2) pm, b = 383.90(8) pm, and c = 702.6(2) pm (Table 1). The lattice parameters reported for the corresponding cerium phase are about 10 % smaller (a = 545.7 pm, b = 342.7 pm, and c = 652.1 pm) [10]. This can be easily explained, because the *in situ* X-ray measurement of the lattice parameters was performed on a compressed structure at 70 GPa, whereas our metastable crystals were measured at ambient pressure conditions.

Looking at the axial ratios of HP-PrO<sub>2</sub>, we obtain values of c/b = 1.83 and a/b = 1.66. These results tally well with the values known for HP-CeO<sub>2</sub> (c/b = 1.9 and a/b = 1.59) [10]. For the differentiation between the  $\delta$ -Ni<sub>2</sub>Si-type and the  $\alpha$ -PbCl<sub>2</sub>-type structure, the parameter a/b is important. For the  $\delta$ -Ni<sub>2</sub>Si type, axial ratios between 1.3 and 1.4 are reported, whereas the a/b ratios for the  $\alpha$ -PbCl<sub>2</sub> type are in the range of 1.5 to 1.75 [10, 33]. Hence, HP-PrO<sub>2</sub> can be classified as an  $\alpha$ -PbCl<sub>2</sub>-type structure. The  $\alpha$ -PbCl<sub>2</sub> structure type contains cations in an almost hexagonal closest-packing, whereas the anions are coordinated tetrahedrally or square-pyramidally, but both distorted [34]. Figure 2 gives an overall view of the structure, showing the coordination of the praseodymium cations.

As listed in Table 2, one praseodymium cation and two oxygen anions can be identified in the structure. The atomic parameters correspond well with the parameters reported for the high-pressure phase of  $CeO_2$  [10]. In Figure 3, the coordination spheres of the oxygen anions are displayed; the dark grey polyhedra indicate tetrahedra, whereas the light grey polyhedra stand for square pyramids.

The praseodymium ion is ninefold coordinated with Pr-O distances ranging from 235.9(2) to 283.7(3) pm (Table 4). These distances are larger than the Pr-O distances of 233.5 pm measured for the ambient-pressure phase of  $PrO_2$ , as expected because of the increase of the coordination number from eight

365



**Figure 2.** HP-PrO<sub>2</sub> in the  $\alpha$ -PbCl<sub>2</sub> structure type.



**Figure 3.** View of the HP-PrO<sub>2</sub> crystal structure along  $[0\bar{1}0]$ . The oxygen ions are either tetrahedrally (dark grey polyhedra) or square-py-ramidally coordinated (light grey polyhedra).

to nine. The Ce–O distances, reported for the orthorhombic HP-CeO<sub>2</sub>, vary between 205.4 and 266.9 pm, being in the same range [10]. The shorter bond lengths in HP-CeO<sub>2</sub> agree with the smaller lattice parameters relative to HP-PrO<sub>2</sub>, because of the *in situ* measurement at 70 GPa.

The two oxygen ions are either fourfold or fivefold coordinated, as displayed in Figure 4. The interatomic angles of the coordination polyhedra are listed in Table 4. For the tetrahedrally coordinated O1 atom, the angles show an average value of 109.2°, very close to the ideal tetrahedral angle. The Pr– O distances lay all between 235.9(2) and 238.3(3) pm, so no distortion of the tetrahedron is found. The coordination sphere of O2 is square-pyramidal. The oxygen atom is located 66.6 pm from the basal plane and slightly shifted towards one side of the pyramid. This results in Pr–O distances of 273.4(3) pm to two neighboring praseodymium ions of the basal plane and of 283.7(3) pm to the other two praseodymium ions. The

distances between the praseodymium ions spanning the basal planes are 381.04(6) and 383.90(8) pm and the angles are 90°, thus the basal plane of the pyramid forms an almost perfect square. The Pr-O bond length between the oxygen ion and the praseodymium ion, which forms the tip of the pyramid, is 245.4(3) pm. If the central atom is located in the center of the pyramid, all Pr-O distances should be equal. This would result in angles of around 85° and 145° between the praseodymium ions of the basal plane [35]. In HP-PrO<sub>2</sub> we find values of 85.2(2), 86.29(3), and 89.2(2)° for the small angle and of 152.3(2)° for the large angle because of the off-center position of the central atom. The angles between the basal plane atoms and the pyramid tip atom should be 108°; in HP-PrO<sub>2</sub>, angles of 98.4(2) and 108.86(9)° are reached. According to the shorter Ce-O-bond lengths in HP-CeO<sub>2</sub>, the coordination polyhedra are smaller than in the HP-PrO<sub>2</sub> phase, but their characteristics are similar.



Figure 4. Tetrahedral and square-pyramidal coordination of the oxygen ions in HP-PrO<sub>2</sub>.

Whereas in the literature no phase transformation of  $PrO_2$  was reported up to 20 GPa at room temperature [20], we obtained the single-crystals of the high-pressure phase at only 5.5 GPa and 1000 °C, starting from a reaction mixture of  $Pr_6O_{11}$ ,  $B_2O_3$ , and  $PrF_3$ . A similar experiment with only  $Pr_6O_{11}$  as a reactant failed in the orthorhombic high-pressure phase. Therefore, probably, the other starting materials took an active part in the phase transition, because of the fact that in  $Pr_6O_{11}$  not every praseodymium cation is in the oxidation state (IV) and thus the reaction to a byproduct influenced the formation of HP-PrO<sub>2</sub>. An experiment with cubic  $PrO_2$  as starting material will therefore be of great interest.

The calculations of the MAPLE value (madelung part of lattice energy according to *Hoppe* [36–38]) resulted in a value of 11225 kJ·mol<sup>-1</sup> for HP-PrO<sub>2</sub>, which is similar to the value of 11987 kJ·mol<sup>-1</sup> of the ambient-pressure phase. The same calculations for the corresponding cerium phases led to 12609 kJ·mol<sup>-1</sup> for HP-CeO<sub>2</sub> and 11948 kJ·mol<sup>-1</sup> for CeO<sub>2</sub>.



#### Conclusions

Under high-pressure/high temperature conditions, crystals of orthorhombic HP-PrO<sub>2</sub> were obtained. A study of the axial ratios of HP-PrO<sub>2</sub> clarified that the high-pressure form of PrO<sub>2</sub> crystallizes in an  $\alpha$ -PbCl<sub>2</sub>-type structure. Whereas phase transformations of the ambient pressure phase previously were not observed up to 20 GPa, in this case the formation of HP-PrO<sub>2</sub> took place at 5.5 GPa and 1000 °C. Starting from a reaction mixture of Pr<sub>6</sub>O<sub>11</sub>, B<sub>2</sub>O<sub>3</sub>, and PrF<sub>3</sub>, single-crystals were obtained, allowing the first single-crystal structure determination of HP-PrO<sub>2</sub>.

## Acknowledgement

We thank *Dr. Gunter Heymann* for collecting the single-crystal data. Special thanks go to *Dipl.-Chem. Marcus Tegel* (LMU Munich) for the robust refinement of the powder data.

#### References

- [1] A. Trovarelli, Catal. Rev. Sci. Eng. 1996, 38, 439-520.
- [2] A. Trovarelli, *Catalysis by Ceria and Related Materials*, Imperial College Press, 2002.
- [3] T. Yamamoto, H. Momida, T. Hamada, T. Uda, T. Ohno, *Thin Solid Film.* 2005, 486, 136–140.
- [4] M. Malchus, M. Jansen, Solid State Sci. 2000, 2, 65-70.
- [5] S. Kern, C.-K. Loong, J. Faber Jr., G. H. Lander, Solid State Commun. 1984, 49, 295–298.
- [6] C. H. Gardiner, A. T. Boothroyd, P. Pattison, M. J. McKelvy, G. J. McIntyre, S. J. S. Lister, *Phys. Rev. B: Condens. Matter* 2004, 70, 024415.
- [7] A. Kotani, T. Jo, J. C. Parlebas, Adv. Phys. 1988, 37, 37-85.
- [8] A. T. Boothroyd, C. H. Gardiner, S. J. S. Lister, P. Santini, B. D. Rainford, L. D. Noailles, D. B. Currie, R. S. Eccleston, R. I. Bewley, *Phys. Rev. Lett.* 2001, *86*, 2082–2085.
- [9] R. Fehrenbacher, T. M. Rice, *Phys. Rev. Lett.* **1993**, *70*, 3471–3474.
- [10] S. J. Duclos, Y. K. Vohra, A. L. Ruoff, A. Jayaraman, G. P. Espinosa, *Phys. Rev. B: Condens. Matter* **1998**, *38*, 7755–7758.
- [11] G. A. Kourouklis, A. Jayaraman, G. P. Espinosa, *Phys. Rev. B: Condens. Matter* **1988**, *37*, 4250–4253.
- [12] L. Gerward, J. Staun Olsen, L. Petit, G. Vaitheeswaran, V. Kanchana, A. Svane, J. Alloys Compd. 2005, 400, 56–61.
- [13] S. E. Hill, C. R. A. Catlow, J. Phys. Chem. Solids 1993, 54, 411– 419.

- [14] D. D. Koelling, A. M. Boring, J. H. Wood, Solid State Commun. 1983, 47, 227–232.
- [15] G. A. Landrum, R. Dronskowski, R. Niewa, F. J. DiSalvo, *Chem. Eur. J.* 1999, 5, 515–522.
- [16] N. V. Skorodumova, R. Ahuja, S. I. Simak, I. A. Abrikosov, B. Johansson, B. I. Lundqvist, *Phys. Rev. B: Condens. Matter* 2001, 64, 115108.
- [17] N. V. Skorodumova, S. I. Simak, B. I. Lundqvist, I. A. Abrikosov, B. Johansson, *Phys. Rev. Lett.* **2002**, *89*, 166601.
- [18] N. V. Skorodumova, M. Baudin, K. Hermansson, *Phys. Rev. B: Condens. Matter* 2004, 69, 075401.
- [19] F. Goubin, X. Racquefelte, M.-H. Whangbo, Y. Montardi, R. Brec, S. Jobic, *Chem. Mater.* 2004, *16*, 662–672.
- [20] L.-G. Liu, Earth Planet. Sci. Lett. 1980, 49, 166-172.
- [21] Z. Hu, S. Bertram, G. Kaindl, Phys. Rev. B: Condens. Matter 1994, 49, 39–43.
- [22] J. Dabrowski, V. Zavodinsky, A. Fleszar, *Microelectron. Reliab.* 2001, 41, 1093–1096.
- [23] D. Walker, M. A. Carpenter, C. M. Hitch, Am. Mineral. 1990, 75, 1020–1029.
- [24] D. Walker, Am. Mineral. 1991, 76, 1092–1100.
- [25] H. Huppertz, Z. Kristallogr. 2004, 219, 330-338.
- [26] D. C. Rubie, Phase Transitions 1999, 68, 431-451.
- [27] N. Kawai, S. Endo, Rev. Sci. Instrum. 1970, 41, 1178-1181.
- [28] K. H. Stone, S. H. Lapidus, P. W. Stephens, J. Appl. Crystallogr. 2009, 42, 385–391.
- [29] Z. Otwinowski, W. Minor, Methods Enzymol. 1997, 276, 307– 326.
- [30] G. M. Sheldrick, SHELXS-97 and SHELXL-97, Program Suite for the Solution and Refinement of Crystal Structures, University of Göttingen, Göttingen, Germany, 1997.
- [31] G. M. Sheldrick, Acta Crystallogr. Sect. A 2008, 64, 112-122.
- [32] W. Jeitschko, Acta Crystallogr. Sect. B 1968, 24, 930-934.
- [33] R. W. G. Wyckoff in *Crystal Structures*, Interscience, New York, 1964.
- [34] H.-J. Meyer in *Moderne Anorganische Chemie* (Ed.: E. Riedel), de Gruyter, Berlin, **2003**.
- [35] J. S. Knyrim, J. Friedrichs, S. Neumair, F. Roessner, Y. Floredo, S. Jakob, D. Johrendt, R. Glaum, H. Huppertz, *Solid State Sci.* 2008, 10, 168–176.
- [36] R. Hoppe, Angew. Chem. 1966, 78, 52–63; Angew. Chem. Int. Ed. Engl. 1966, 5, 95–106.
- [37] R. Hoppe, Angew. Chem. 1970, 82, 7–16; Angew. Chem. Int. Ed. Engl. 1970, 9, 25–34.
- [38] R. Hübenthal, MAPLE (Version 4), Program for the Calculation of MAPLE Values, University of Gießen, Gießen, Germany, 1993.

Received: September 13, 2009 Published Online: October 30, 2009