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$Gd_4(BO_2)O_5F$ – a gadolinium borate fluoride oxide comprising a linear BO_2 moiety

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Abstract: Gadolinium borate fluoride oxide $Gd_4(BO_2)O_5F$ crystallises in space group *Pmmn* (no. 59, a = 1574.6(4), b = 381.42(7), c = 660.88(11) pm, 565 refl., 28 parameters, R_1 = 0.039, wR_2 = 0.128, twin refinement) and comprises linear BO_2^- anions between closely packed [GdO] layers formed by OGd_4 tetrahedra and terminated by oxygen and fluorine atoms. The crystal structure's relationship with the NiAs type is illustrated. The Raman spectrum recorded on a single crystal of $Gd_4(BO_2)O_5F$ comprises a single peak at 1364 cm^{-1} assigned to the only Raman-active vibrational mode ν_s of the linear triatomic O–B–O units besides very weak peaks at 805 and 2083 cm^{-1} (presumably the respective δ and ν_{as} modes).

Keywords: borate; crystal structure; gadolinium; single crystal.

Dedicated to Prof. Dr. Harald Hillebrecht.

1 Introduction

In the course of our systematic investigations of host structures for luminescence applications or even luminescent compounds [1] we focused on phosphates like α-$Sr(PO_3)_2$ [2, 3] or $Gd(PO_3)_3$ [4, 5], on boro-phosphates like $(NH_4)_2Mn[B_2P_3O_{11}(OH)_2]Cl$ [6], novel classes of crystalline boro-sulphates [7–10] and fluoroborates [11], and on borate fluorides like $Eu_5(BO_3)_3F$ [12]. The latter contains an emitter ion already and compounds containing trivalent gadolinium transparent in the visible regime are therefore also good candidates for luminescence applications. Fluoride borates of gadolinium described so far are $Gd_2(BO_3)F_3$ [13, 14], $Gd_3(BO_3)_2F_3$ [14] and $Gd_4[B_4O_{11}]F_2$ [15]. Like $Eu_5(BO_3)_3F$, all of them comprise trigonally planar borate ions; in $Gd_4[B_4O_{11}]F_2$ an unprecedented B_4O_{11} moiety consisting of three corner-sharing BO_4 tetrahedra and a trigonally planar BO_3 unit has been detected.

Molecular moieties with the 'magic' number of 16 electrons fascinated chemists at all times. Like carbon dioxide, all isoelectronic ions like azide N_3^-, cyanate OCN^-, fulminate CNO^-, nitridoborate BN_2^{3-} or nitronium NO_2^+ form linear triatomic units. Relatively new to this family are carbidoborate CBC^{5-} [16] anions comprising the highest negative charge found so far for such moieties. A more common example should be the simple borate BO_2^-, but this anion was postulated only once to be present in the channels of *apatite*-type compounds $(Ca,Sr)_{9+y}Na_x(BO_2)_{x+2y}(PO_4)_6$ with $x + 2y < 1$ [17] where the oxygen positions of the assumed BO_2^- anion coincide with those of two adjacent OH^- anions inside the hexagonal channels.

In this manuscript I present the results of the crystal structure analysis of presumably systematically twinned crystals of a new gadolinium borate fluoride oxide and first spectroscopic data to prove the presence of linear BO_2^- anions.

2 Results and discussion

2.1 Crystal structure determination

The diffraction pattern suggested a hexagonal unit cell (a = 381, c = 1573 pm) with reflection conditions pointing towards space group $P6_3/mmc$ (no. 194). Since the structure model solved and refined in this space group comprised exactly semi-occupied boron positions and further disorder, a careful inspection of the diffraction images was performed which revealed very weak superstructure reflections. Taking into account these additional reflections a primitive orthorhombic unit cell with an approximate ratio $b/a \approx 1.733 \approx \sqrt{3}$ was indexed (a = 381.42(7), b = 660.88(11), c = 1574.6(4) pm). This special b/a ratio yielded by threefold partially merohedrally twinning a *drilling* dissembling the above mentioned hexagonal unit cell; the reflections breaking the C centring of the orthohexagonal unit cell are the aforementioned weak

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superstructure reflections. The final twin refinement was performed in space group *Pmmn* (no. 59, $a = 1574.6(4)$ pm, $b = 381.42(7)$ pm, $c = 660.88(11)$ pm) which delivered the most stable and reliable structure refinement after a careful check for the presence or absence of an inversion centre by refining and analysing the structure model in respective space groups like e.g. $Pmn2_1$. Relevant data of the crystal structure determination are listed in Table 1, selected interatomic distances and bond angles are given in Table 2. The assignment of oxygen and fluorine was decided in combination with MAPLE calculations, interatomic distances and considerations based on Pauling's rules (see below).

2.2 Crystal structure

Nickel arsenide crystallises in space group $P6_3/mmc$ (no. 194, ratio $c/a \approx 1.39$) [18]. The initially found hexagonal unit cell features a very similar ratio $c/3a \approx 1.376$ suggesting a close relationship of the title compound's crystal structure with that of nickel arsenide. By this relationship the crystal structure of $Gd_4(BO_2)O_5F$ and also the observed twinning as a *drilling* may be understood and followed using the group-subgroup scheme in the Bärnighausen formalism [19–22] shown in Fig. 1. It starts with the structural data of NiAs including subsequently occupied tetrahedral and trigonal prismatic voids on Wyckoff positions *4f* and *2b*. Tripling along [001] yields already the dimensions of the previously mentioned hexagonal unit cell. A suited example adopting a similar structure is $InGaZn_2O_5$ [23] showing linearly coordinated gallium atoms between ZnO layers, illustrated by the notation $In[ZnO]_2[GaO_2]O$. Compared with the title compound, i.e. $[GdO]_4[BO_2]OF$ in this notation, the site of Ga(1) adopts that of the boron atoms, but in contrast to the title compound this site is fully occupied in $InGaZn_2O_5$ in $P6_3/mmc$. After transformation to the orthohexagonal cell in *Cmcm* (no. 63) three different orientations of the resulting structure are possible, presumably yielding the twinning during crystal growth. By loosing the *C* centring the final space group *Pmmn* (no. 59) is reached where the respective Ga(1) site of $InGaZn_2O_5$ splits and a fully occupied site B(1) is achieved.

Table 1: Crystal structure data for $Gd_4(BO_2)O_5F$.

Formula	$Gd_4(BO_2)O_5F$
M_r	770.81
Cryst. size, mm^3	$0.09 \times 0.07 \times 0.04$
Crystal system	Orthorhombic
Space group	*Pmmn*
a, Å	15.746(4)
b, Å	3.8142(7)
c, Å	6.6088(11)
V, Å^3	396.91(14)
Z	2
D_{calcd}, g cm^{-3}	6.45
$\mu(MoK_\alpha)$, cm^{-1}	33.0
F(000), e	652
hkl range	±20, ±4, $-8 \rightarrow +7$
θ range, deg	3.08–27.5
Refl. measured/unique/R_{int}	3171/565/0.102
Param. refined	28
$R(F)^a/wR(F^2)^b$ (all reflexions)	0.039/0.128
twin components	0.32(2)/0.31(2)/0.37(2)
GoF $(F^2)^c$	0.886
$\Delta\rho_{fin}$ (max/min), e Å^{-3}	1.78/−2.50

$^a R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $^b wR(F^2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + (0.0730\,P)^2]^{-1}$, where $P = (\mathrm{Max}(F_o^2, 0) + 2F_c^2)/3$; ^{c} GoF $= [\Sigma w(F_o^2 - F_c^2)^2/(n_{obs} - n_{param})]^{1/2}$.

Table 2: Selected interatomic distances (Å) and angles (deg) with estimated standard deviations in parentheses.

Distances	
Gd–O	2.274(11)–2.536(15)
Gd–O/F	2.484(17)–2.56(3)
B–O	1.213(1)
Angles	
O–B–O	180(2)
Gd–O–Gd	104.7(8)–114.0(9)

The crystal structure of $Gd_4(BO_2)O_5F$ is composed of dense layers $^2_\infty[OGd_{4/4}]$ formed by edge-sharing $[OGd_4]$ tetrahedra terminated by fluorine and further oxygen atoms. Between these oxygen atoms the boron atoms are part of linear BO_2^- anions (Fig. 2) located in trigonal prismatic voids (Fig. 3a). The bond length B–O was refined to 121.3 pm and the angle O–B–O to a value of 180(4)° in accordance with the expectation for a moiety isolectronic with CO_2 (115 pm, 180° [24]) and NO_2^+ (108–114 pm, avg. 111 pm, 175–180° [25–27]); the sum of ionic radii cannot be calculated due to the lack of an ionic radius for linearly coordinated B^{3+}. Calvo and Faggiani found a bond length of 125(2) pm in $(Ca,Sr)_{9+y}Na_x(BO_2)_{x+2y}(PO_4)_6$ $(x + 2y < 1)$ [17]. The coordination polyhedron around both gadolinium atoms shown in Fig. 3b can be described as a tricapped tetrahedron comprising coordination distances between 233 and 256 pm (Gd1) and between 227 and 248 pm (Gd2). These distances are also in agreement with the sum of the ionic radii of 238 pm [28]. Selected interatomic distances and bond angles are listed in Table 2.

2.3 Electrostatic calculations

The electrostatic consistency of the structure model was proved by calculations based on the MAPLE concept

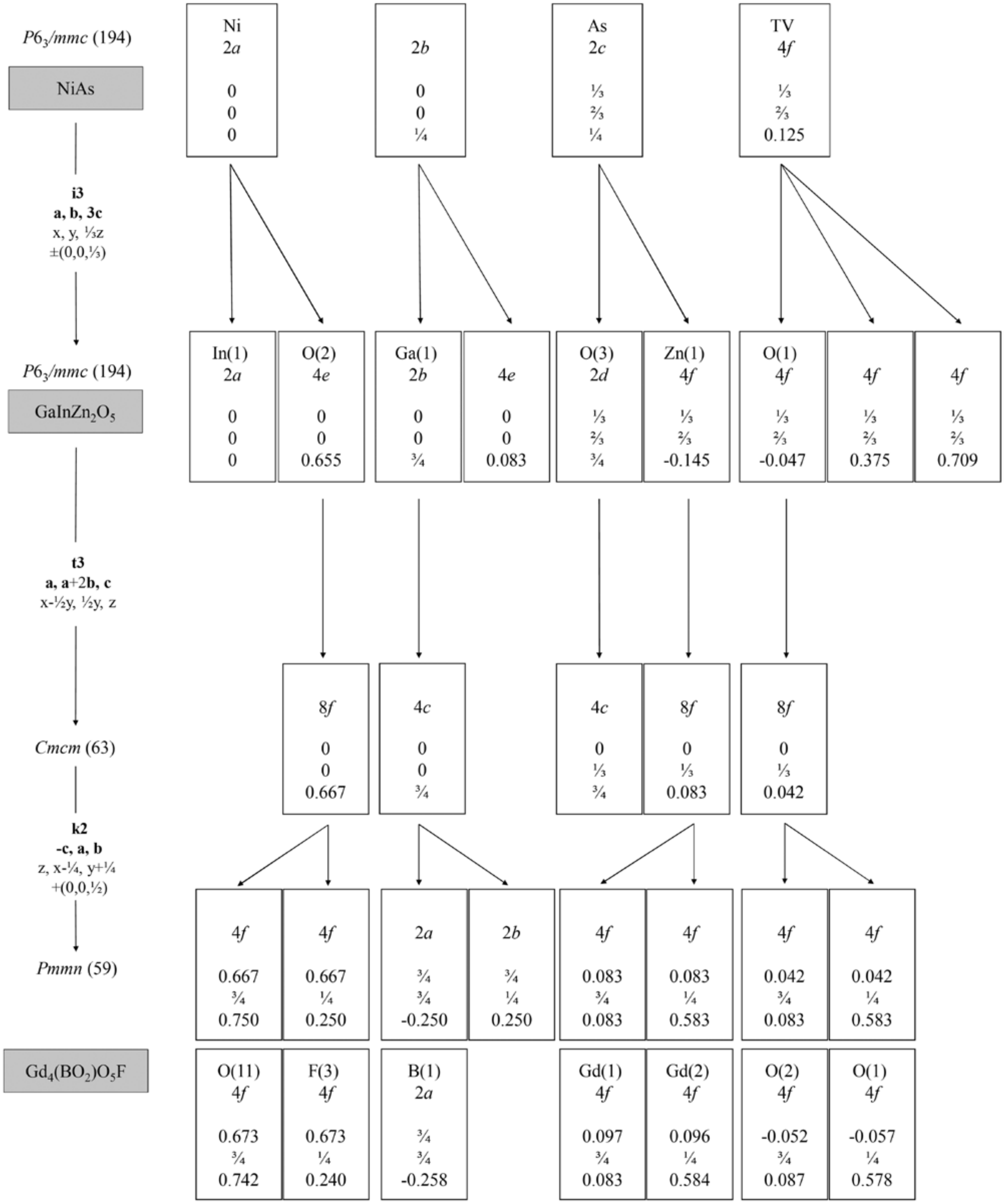

Fig. 1: Group–subgroup scheme in the Bärnighausen formalism [19–22] showing the symmetry relations between NiAs, $InGaZn_2O_5$ and $Gd_4(BO_2)O_5F$ (at the last stage of the scheme also the calculated coordinates derived from the NiAs type are shown).

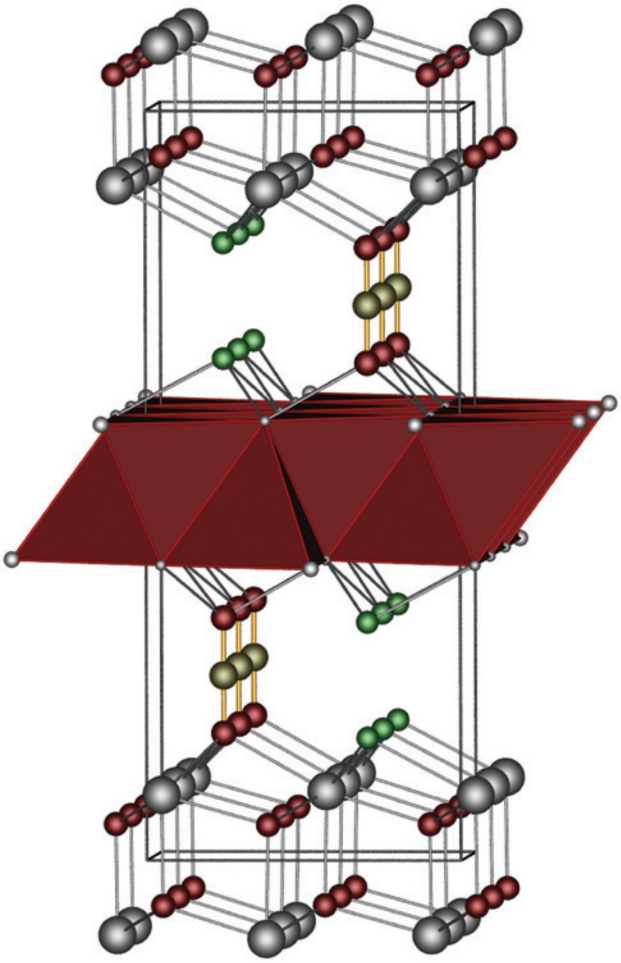

Fig. 2: Perspective view of the crystal structure of $Gd_4(BO_2)O_5F$ approx. along [010] illustrating the layer of OGd_4 tetrahedra (shown as closed tetrahedra); Gd atoms grey, boron brown, fluorine green and oxygen red.

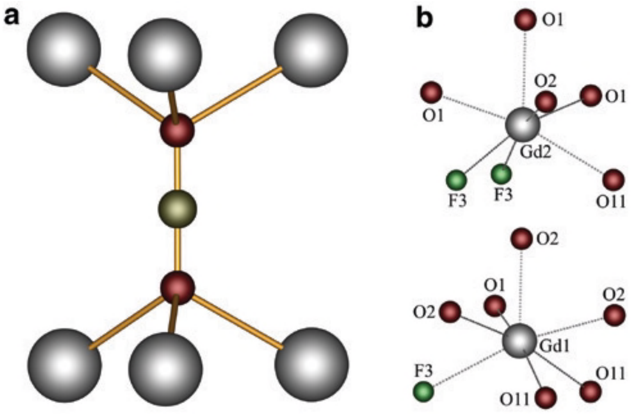

Fig. 3: Local surroundings of the linear BO_2^- moiety and the metal ions. (a) The BO_2^- anion in its trigonal prismatic void; (b) coordination spheres of the gadolinium atoms (site symmetry *.m.* for Gd1 and Gd2) viewed along [001]; same colour code as in Fig. 1.

Table 3: MAPLE calculations for $Gd_4(BO_2)O_5F$.

$Gd_4(BO_2)O_5F$	⅓($Gd_2(BO_3)F_3$ [13] + B_2O_3 [32] + 5Gd_2O_3 [33])
MAPLE = 39 079 kJ mol^{-1}	MAPLE = 39 457 kJ mol^{-1}
	$\Delta = 0.97$ %

(*M*adelung *P*art of *L*attice *E*nergy) [29–31]. A structure model is electrostatically consistent if the sum of MAPLE values of chemically similar compounds like $Gd_2(BO_3)F_3$ [13], B_2O_3 [32] and *C*-type Gd_2O_3 [33] deviates from the MAPLE value of the compound of interest, i.e. $Gd_4(BO_2)O_5F$, by less than approx. 1 %. According to our calculations, the structure model of $Gd_4(BO_2)O_5F$ thus shows electrostatic consistency as presented in Table 3.

Based on X-ray single-crystal data an unequivocal assignment of oxygen and fluorine atoms to respective sites is difficult; therefore all reasonable models of O/F ordering on the different sites have been investigated by these calculations which have proven to give reliable assignments for the assignment of oxygen and nitrogen to their respective sites in oxonitridosilicates [34, 35]. Indeed, the calculations for $Gd_4(BO_2)O_5F$ gave significantly different Madelung parts of lattice energy as well as striking differences of partial Madelung factors leading to the final assignment of fluorine solely to site F3 which accordingly is occupied 1:1 by oxygen and fluorine. This site is also the most probable one with regard to Pauling's rules as it provides the smallest possible coordination number the fluorine atoms may experience in $Gd_4(BO_2)O_5F$.

2.4 Raman spectroscopy

Figure 4 shows the relevant region of the Raman spectrum recorded on a single crystal of $Gd_4(BO_2)O_5F$. It comprises a single intense peak at 1364 cm^{-1}. The only Raman-active vibrational mode in linear three-atomic molecules Y–X–Y (atom types X and Y) is the symmetric stretching mode. In cationic NO_2^+ this vibration was recorded at 1396 cm^{-1} [36], in neutral CO_2 at 1388 cm^{-1} [36]; for the anionic species BN_2^{3-} and BC_2^{5-} this vibration was excited in the range 1028 and 1107 cm^{-1} [37] and at 1041 cm^{-1} [16], respectively. Considering the obvious trend that with decreasing atomic mass of Y and increasing negative charge the excitation energies also decrease, the Raman peak at 1364 cm^{-1} is in line with observations and theoretical considerations on 16-electron molecular moieties [38]. Moreover, very weak peaks were observed at 805 and 2083 cm^{-1}, which presumably are due to the respective IR active δ and ν_{as} modes.

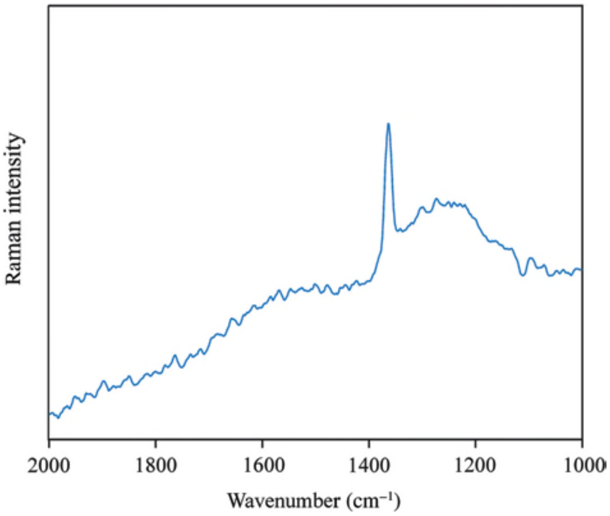

Fig. 4: Relevant region of a Raman spectrum recorded of a single-crystal of $Gd_4(BO_2)O_5F$ showing the Raman-active vibration.

3 Experimental section

3.1 Synthesis of $Gd_4(BO_2)O_5F$

Under argon, a homogenised mixture of Gd_2O_3 (236 mg, 0.651 mmol, ChemPur, 99.99 %), B_2O_3 (22 mg, 0.32 mmol, ChemPur, 99.9 %) and NaF (15 mg, 0.36 mmol, ChemPur, 99.9 %) was transferred into a boron nitride crucible which was then enclosed in a sealed tantalum ampoule; the reaction was performed under a constant argon flow by applying the following temperature program: the reaction mixture was heated to 800 °C at a rate of 480 °C/h, subsequently heated further to 1500 °C at a rate of 120 °C h^{-1}, and this temperature was held for 72 h. After cooling to room temperature at a rate of 30 °C h^{-1}, some colourless crystals of $Gd_4(BO_2)O_5F$ were obtained as a side product; by means of energy dispersive X-ray spectroscopy (EDX) Gd was detected as the only metal present in the single crystals.

3.2 X-ray structure determination

X-Ray diffraction data were collected from two carefully selected single crystals enclosed in a Lindemann tube on a Stoe IPDS 2 diffractometer using MoK_α radiation and – in the case of the HKLF4 integration – corrected numerically for absorption [39]. The crystal structure of the title compound was solved by direct methods and subsequently refined in space group *Pmmn* (no. 59, a = 1574.6(4), b = 381.42(7), c = 660.88(11) pm) using the SHELXTL program package [40] based on HKLF5 and HKLF4 data.

The relevant crystallographic data and further details of the X-ray data collection are summarised in Table 1. In Table 2 selected interatomic distances and bondangles are listed. Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-informationsdienste.de/en/DB/icsd/depot_anforderung.html) on quoting the deposition number CSD-429779.

3.3 Raman spectroscopy

The Raman spectrum was recorded using a spectrometer comprising a double monochromator and different excitation lasers (krypton, argon and Ti:sapphire, 90° and 180° geometry), providing excitations in the range 330–830 nm, equipped with a cryostat (15–330 K) and a heating stage for high-temperature measurements up to 1000 K.

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