

# Single-crystal Structure Determination and Spectroscopic Characterization of $\text{KSr}_4(\text{BO}_3)_3$

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*Z. Naturforsch.* **2013**, 68b, 338–344 / DOI: 10.5560/ZNB.2013-3074

Received February 15, 2013

During attempts to synthesize a high-pressure phase of  $\text{KSr}_4(\text{BO}_3)_3$  using pressures of up to 12 GPa, single crystals of the normal-pressure phase  $\text{KSr}_4(\text{BO}_3)_3$  with sufficient quality for single-crystal diffraction experiments could be obtained at 3 GPa and 1300 °C in a Walker-type multi-anvil apparatus. The single-crystal structure determination verified the published powder diffraction data of  $\text{KSr}_4(\text{BO}_3)_3$  revealing the non-centrosymmetric space group *Ama2* with  $a = 1104.8(2)$ ,  $b = 1199.1(2)$ ,  $c = 688.8(2)$  pm and  $Z = 4$ . Additionally, IR- and Raman-spectroscopic investigations were performed on single crystals of the compound.

**Key words:** High Pressure, Borate, Crystal Structure, Raman Spectroscopy, IR Spectroscopy

## Introduction

In 2006, the compounds  $\text{NaCa}_4(\text{BO}_3)_3$ ,  $\text{KCa}_4(\text{BO}_3)_3$  and  $\text{KSr}_4(\text{BO}_3)_3$  were synthesized by Wu *et al.* in order to find new deep-UV non-linear optical (NLO) and birefringent materials [1]. As synthesis route, sintering of the alkali metal and alkaline earth metal carbonates together with boric acid at temperatures up to 900 °C was chosen. Interestingly, only powder samples were received by this route, hence the structure refinements were merely performed on the basis of powder diffraction data. Since the Rietveld refinements of  $\text{NaCa}_4(\text{BO}_3)_3$  and  $\text{KCa}_4(\text{BO}_3)_3$  started from the structural model of  $\text{KSr}_4(\text{BO}_3)_3$ , a verification of the structure solution and refinement of  $\text{KSr}_4(\text{BO}_3)_3$  based on single-crystal diffraction data is of importance.

According to the structure solution and refinement by Wu *et al.* [1], the structure of all three compounds consists of trigonal-planar  $\text{BO}_3$  groups and of alkali metal cations surrounded by eight oxygen atoms in the form of a bicapped trigonal prism. The earth alkaline atoms are found in three different crystallographic positions coordinated to eight or nine oxygen atoms. Due to the fact that no tetrahedral  $\text{BO}_4$  groups are present in the structure of  $\text{KSr}_4(\text{BO}_3)_3$ , the use of high-pressure conditions could transform the trigonal  $\text{BO}_3$

groups into tetrahedral  $\text{BO}_4$  units leading to a new high-pressure phase of  $\text{KSr}_4(\text{BO}_3)_3$ . This paper reports about the attempts to synthesize a high-pressure phase of  $\text{KSr}_4(\text{BO}_3)_3$ , which were unsuccessful up to a pressure of 12 GPa. Nevertheless, as the parameter pressure favors the crystallization of borates [2], it was possible to receive single crystals of the normal-pressure phase  $\text{KSr}_4(\text{BO}_3)_3$  for the first time. Next to a comparison of the single-crystal data with the powder data of Wu *et al.* [1], we report about ATR-IR and Raman spectroscopic measurements on single crystals of  $\text{KSr}_4(\text{BO}_3)_3$ .

## Experimental Section

### Synthesis

$\text{KSr}_4(\text{BO}_3)_3$  was obtained from a two-stage synthesis. In the first step, a precursor was produced by a high-temperature synthesis according to the published synthesis route. A stoichiometric mixture of 0.44 mmol  $\text{K}_2\text{CO}_3$  (Strem Chemicals, Newburyport/USA), 3.54 mmol  $\text{SrCO}_3$  (Merck KGaA, Darmstadt/Germany) and 2.64 mmol  $\text{H}_3\text{BO}_3$  (Schering-Kahlbaum AG, Berlin/Germany) was ground together in an agate mortar and filled into a FKS 95/5 (Feinkornstabilisiert, 95 % Pt, 5 % Au) crucible (No. 21, Ögussa, Wien/Austria). The mixture was heated to 600 °C in 6 h to decompose the carbonates and the boric acid. The temperature was kept at 600 °C for 1 h and afterwards raised

to 900 °C in 3 h. After two days, the reaction mixture was quenched by removing the crucible from the oven. The powder diffraction pattern showed  $\text{KSr}_4(\text{BO}_3)_3$  and  $\text{Sr}_3\text{B}_2\text{O}_6$  [3], the latter as a side phase. An attempt to remove  $\text{Sr}_3\text{B}_2\text{O}_6$  by annealing the ground sample at 900 °C (heating with 300 °C h<sup>-1</sup>) was not successful, so the product was finely ground and used for the second step of the synthesis.

For the high-pressure experiments, the product was filled into a crucible made of hexagonal boron nitride (HeBoSint® P100, Henze BNP GmbH, Kempten, Germany), built into an 18/11-assembly and compressed by eight tungsten carbide cubes (TSM-10, CERATIZIT Austria GmbH, Reutte/Austria). A hydraulic press (mavo press LPR 1000-400/50, Max Voggenreiter GmbH, Mainleus/Germany) and a Walker-type module (also Max Voggenreiter GmbH) were used to apply the pressure. Details of the assembly and its preparation are described in the references [4–8]. For the synthesis of single-crystals of  $\text{KSr}_4(\text{BO}_3)_3$ , the precursor was compressed to 3 GPa within 1.5 h and kept at this pressure during the heating period. The sample was heated to 1300 °C in 10 min and kept there for 10 min. After cooling to 350 °C within 60 min, the reaction mixture was quenched to room temperature by turning off the heating. The decompression of the assembly lasted 11 h. The octahedral pressure medium (MgO, Ceramic Substrates & Components Ltd., Newport, Isle of Wight/UK) was recovered and broken apart. The sample was separated from the surrounding boron nitride crucible and yielded as colorless polycrystalline block. The colorless crystals were found to be  $\text{KSr}_4(\text{BO}_3)_3$ .

#### Crystal structure analysis

The powder diffraction pattern was obtained in transmission geometry, using a Stoe Stadi P powder diffractometer with Ge(111)-monochromatized  $\text{MoK}_\alpha$  radiation ( $\lambda = 70.93$  pm). The diffraction pattern showed the reflections of  $\text{KSr}_4(\text{BO}_3)_3$  along with four weak, unidentified reflections. Fig. 1 (top) shows the experimental powder pattern that matches well with the theoretical pattern (bottom) simulated from the single-crystal data. Single crystals of  $\text{KSr}_4(\text{BO}_3)_3$  were isolated by mechanical fragmentation. The single-crystal intensity data were collected at room temperature using a Nonius Kappa-CCD diffractometer with graphite-monochromatized  $\text{MoK}_\alpha$  radiation ( $\lambda = 71.073$  pm). A semi-empirical absorption correction based on equivalent and redundant intensities (SCALEPACK [9])

was applied to the intensity data. All relevant details of the data collection and evaluation are listed in Table 2. The space groups  $\text{Cmc}2_1$ ,  $\text{Cmcm}$  and  $\text{Ama}2$  were derived from the systematic extinctions. Since solutions and refinements in the space group  $\text{Cmc}2_1$  and  $\text{Cmcm}$  were not successful, the structural refinement was performed with the positional parameters of the published powder diffraction data as starting values in the space group  $\text{Ama}2$  (SHELXL-97 [10, 11] [full-matrix least-squares on  $F^2$ ]). All atoms were refined with anisotropic displacement parameters, and the final difference Fourier syntheses did not reveal any significant peaks. Tables 3–6 list the positional parameters, anisotropic displacement parameters, selected interatomic distances and angles.

Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; E-mail: [crysdata@fiz-karlsruhe.de](mailto:crysdata@fiz-karlsruhe.de), [http://www.fiz-informationsdienste.de/en/DB/icsd/depot\\_anforderung.html](http://www.fiz-informationsdienste.de/en/DB/icsd/depot_anforderung.html)) on quoting the deposition number CSD-425548.

#### Vibrational spectroscopy

The ATR-FT-IR (Attenuated Total Reflection) spectra of single crystals of  $\text{KSr}_4(\text{BO}_3)_3$  were measured in the spectral range of 600–4000 cm<sup>-1</sup> (spectral resolution: 4 cm<sup>-1</sup>) with a Vertex 70 FT-IR spectrometer (Bruker Optik GmbH, Ettlingen/Germany), equipped with a MCT (Mercury Cadmium Telluride) detector and attached to a Hyperion 3000 microscope (Bruker Optik GmbH). As mid-infrared source, a Globar (silicon carbide) rod was used. A frustum-shaped germanium ATR-crystal with a tip diameter of 100  $\mu\text{m}$  was pressed on the surface of the borate crystal crushing it into small pieces of  $\mu\text{m}$ -size. 128 scans of the sample were acquired. A correction for atmospheric influences using the OPUS 6.5 software was performed.

The single-crystal Raman spectrum of  $\text{KSr}_4(\text{BO}_3)_3$  was measured in the spectral range of 50–1700 cm<sup>-1</sup> with a Raman micro-spectrometer LabRAM HR-800 (HORIBA Jobin Yvon GmbH, Bensheim/Germany) and hundredfold magnification. As excitation source, an Nd:YAG laser ( $\lambda = 532.22$  nm) was used. To avoid a destruction of the crystal, the laser beam was weakened by a D 0.6 filter. The Raman-scattered light was detected through an optical grid with 1800 lines mm<sup>-1</sup>. Four ranges were measured with a spec-

$\text{K}_2\text{CO}_3$	:	$\text{SrCO}_3$	:	$\text{H}_3\text{BO}_3$	$p$ (GPa)	$T$ (°C)	Products
1	:	8	:	6	ambient pressure	900	microcrystalline $\text{KSr}_4(\text{BO}_3)_3$ , $\text{Sr}_3\text{B}_2\text{O}_6$ [3]
1	:	8	:	6	3	1300	cryst. $\text{KSr}_4(\text{BO}_3)_3$ , BN (from crucible)
1	:	8	:	6	7.5	1300	cryst. $\text{KSr}_4(\text{BO}_3)_3$ , $\text{Sr}_3\text{B}_2\text{O}_6$ [3]
1	:	8	:	6	12	1300	cryst. $\text{KSr}_4(\text{BO}_3)_3$ , $\text{SrB}_2\text{O}_4$ -IV [12], $\text{H}_3\text{BO}_3$ [13]

Table 1. Performed syntheses of  $\text{KSr}_4(\text{BO}_3)_3$  with reaction conditions (molar ratios,  $p$ ,  $T$ ) and resulting products.

Table 2. Crystal data and structure refinement of  $\text{KSr}_4(\text{BO}_3)_3$  with standard deviations in parentheses.

Empirical formula	$\text{KSr}_4(\text{BO}_3)_3$
Molar mass, $\text{g mol}^{-1}$	566.01
Crystal system	orthorhombic
Space group	<i>Ama2</i> (no. 40)
Single-crystal diffractometer	Enraf-Nonius Kappa CCD
Radiation; wavelength, pm	$\text{Mo K}\alpha$ ; 71.073 (graphite monochromator)
Lattice parameters {powder data from ref. [1]}	
<i>a</i> , pm	1104.8(2) {1103.843(8)}
<i>b</i> , pm	1199.1(2) {1198.974(9)}
<i>c</i> , pm	688.8(2) {688.446(5)}
<i>V</i> , Å <sup>3</sup>	912.5(3) {911.14(2)}
Formula units per cell, <i>Z</i>	4
Calculated density, $\text{g cm}^{-3}$	4.12
Crystal size, mm <sup>3</sup>	$0.10 \times 0.08 \times 0.06$
Temperature, K	293
Absorption coefficient, $\text{mm}^{-1}$	23.7
<i>F</i> (000), e	1032
$\theta$ range, deg	3.4–37.8
Range in <i>hkl</i>	$-16 \leq h \leq 19$ ; $-20 \leq k \leq 20$ ; $-11 \leq l \leq 10$
Reflections total / independent / <i>R</i> <sub>int</sub>	7697 / 2451 / 0.0588
Reflections with $I > 2\sigma(I)/R_\sigma$	2361 / 0.0444
Data / ref. parameters	2451 / 89
Absorption correction	Multi-scan (SCALEPACK [9])
Goodness-of-fit on <i>F</i> <sub>i</sub> <sup>2</sup>	1.063
Flack parameter <i>x</i>	0.03(2)
Final <i>R</i> <sub>1</sub> / <i>wR</i> <sub>2</sub> [ $I > 2\sigma(I)$ ]	0.0329 / 0.0814
<i>R</i> <sub>1</sub> / <i>wR</i> <sub>2</sub> (all data)	0.0345 / 0.0826
Largest diff. peak / hole, e Å <sup>-3</sup>	2.68 / -1.23

tral resolution better than  $2 \text{ cm}^{-1}$ . The measurement time per step was 80 s. A background correction was applied.

## Results and Discussion

### Synthetic conditions

$\text{KSr}_4(\text{BO}_3)_3$  was synthesized at different pressures (3 GPa/1300 °C, 7.5 GPa/1300 °C and 12 GPa/1300 °C). With increasing pressure, the crystallinity decreased, and the amount of specific crystalline side phases increased. From the experiment at 3 GPa, only hexagonal BN from the crucible could be identified as a side phase in the powder pattern (see Fig. 1), while  $\text{Sr}_3\text{B}_2\text{O}_6$  [3] was found in the powder pattern of the synthesis at 7.5 GPa. The syntheses at 12 GPa led to the high-pressure phase  $\text{SrB}_2\text{O}_4(\text{IV})$  [12] and  $\text{H}_3\text{BO}_3$  [13] as side phases. A detailed protocol of the performed syntheses including reaction conditions and products is shown in Table 1.

Table 3. Atomic coordinates and equivalent isotropic displacement parameters  $U_{\text{eq}}$  (Å<sup>2</sup>) of  $\text{KSr}_4(\text{BO}_3)_3$  (space group: *Ama2*) with standard deviations in parentheses.  $U_{\text{eq}}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor. The standardized atomic coordinates from Pearson's crystal data base entry # 1211921 [31] (standard deviations of the published data in parentheses) and  $U_{\text{iso}}$  from the powder data [1] are listed in italics for comparison.

Atom	Wyckoff	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}/U_{\text{iso}}$
Sr1	4 <i>b</i>	1/4	0.14556(4)	0.65333(6)	0.00823(9)
		1/4	0.1449(2)	0.6523(5)	0.0080(5)
Sr2	8 <i>c</i>	0.02929(3)	0.21499(2)	0.01973(5)	0.00754(8)
		0.0293(1)	0.2148(1)	0.0197(4)	0.0082(3)
Sr3	4 <i>a</i>	0	0	0.37213(7)	0.01008(9)
		0	0	0.3729	0.0107(5)
K	4 <i>b</i>	1/4	0.4164(2)	0.4175(2)	0.0202(2)
		1/4	0.4156(5)	0.4205(9)	0.016(1)
O1	4 <i>b</i>	1/4	0.1471(3)	0.0363(6)	0.0118(6)
		1/4	0.153(2)	0.044(3)	0.004(4)
O2	4 <i>b</i>	1/4	0.4545(4)	0.9887(7)	0.180(8)
		1/4	0.429(2)	0.002(3)	0.041(3)
O3	8 <i>c</i>	0.6416(2)	0.1660(2)	0.2675(4)	0.0103(4)
		0.636(1)	0.1727(9)	0.257(2)	0.005(3)
O4	8 <i>c</i>	0.0254(2)	0.5974(2)	0.2026(4)	0.0105(4)
		0.0302(7)	0.5983(9)	0.199(2)	0.003(2)
O5	8 <i>c</i>	0.1417(2)	0.1865(2)	0.3333(4)	0.0108(4)
		0.142(2)	0.1982(8)	0.331(2)	0.005(3)
O6	4 <i>a</i>	0	0	0.0017(6)	0.0136(7)
		0	0	0	0.010(4)
B1	4 <i>b</i>	1/4	0.3753(5)	0.8470(8)	0.0099(8)
		1/4	0.357(2)	0.841(4)	0.001(6)
B2	4 <i>b</i>	1/4	0.1704(5)	0.2322(8)	0.0088(8)
		1/4	0.172(2)	0.240(4)	0.004(6)
B3	4 <i>a</i>	0	0	0.8032(8)	0.0079(7)
		0	0	0.800(5)	0.015(7)

### Crystal structure of $\text{KSr}_4(\text{BO}_3)_3$

The refinement based on single-crystal data presented here confirms the cell parameters of the published powder data refinement [1] (see Table 2). Nevertheless, some of the atomic coordinates differ as compared in Table 3. This new set of atomic coordinates based on single-crystal data leads to more precise values for bond lengths and angles.

The structure of  $\text{KSr}_4(\text{BO}_3)_3$  is built up from isolated, planar  $\text{BO}_3$  groups as shown in Fig. 2. The B–O bond lengths within these groups vary between 136.2(7) and 140.6(4) pm with an average value of 138.7 pm (see Table 5) with O–B–O angles distributed from 116.7(5) to 121.6(2)° (average value: 120°) (see Table 6). The mean values of the B–O distances correspond well with the known average values for B–O distances in  $\text{BO}_3$  groups (137.0 pm) [14]. Com-

Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Sr1	0.0063(2)	0.0091(2)	0.0093(2)	0.0000(2)	0	0
Sr2	0.0070(2)	0.0078(2)	0.0079(2)	0.00053(9)	0.00004(9)	0.00078(8)
Sr3	0.0150(2)	0.0067(2)	0.0085(2)	0	0	0.0002(2)
K	0.0142(4)	0.0191(5)	0.0274(6)	0.0071(4)	0	0
O1	0.010(2)	0.016(2)	0.009(2)	−0.003(2)	0	0
O2	0.015(2)	0.018(2)	0.022(2)	−0.010(2)	0	0
O3	0.0072(9)	0.010(1)	0.014(2)	0.0006(8)	−0.0008(8)	−0.0001(7)
O4	0.017(2)	0.0061(9)	0.009(2)	0.0007(8)	0.0000(8)	−0.0006(8)
O5	0.0063(9)	0.016(2)	0.010(1)	0.0005(8)	0.0011(7)	0.0017(8)
O6	0.023(2)	0.011(2)	0.007(2)	0	0	−0.005(2)
B1	0.008(2)	0.011(2)	0.011(2)	0.003(2)	0	0
B2	0.005(2)	0.010(2)	0.011(2)	0.001(2)	0	0
B3	0.008(2)	0.011(2)	0.006(2)	0	0	0.000(2)

Table 4. Anisotropic displacement parameters ( $\text{\AA}^2$ ) of  $\text{KSr}_4(\text{BO}_3)_3$  (space group: *Ama2*) with standard deviations in parentheses.

Sr1–O5a	255.6(3)	Sr2–O5a	251.5(3)	Sr3–O6	255.1(4)	K–O3a	286.7(3)
Sr1–O5b	255.6(3)	Sr2–O3a	256.8(3)	Sr3–O4a	257.4(3)	K–O3b	286.7(3)
Sr1–O2	255.6(4)	Sr2–O5b	257.2(3)	Sr3–O4b	257.4(3)	K–O1	288.5(4)
Sr1–O4a	257.0(3)	Sr2–O1	257.3(1)	Sr3–O3a	263.2(3)	K–O2	298.8(5)
Sr1–O4b	257.0(3)	Sr2–O4a	260.0(3)	Sr3–O3b	263.2(3)	K–O6a	299.5(1)
Sr1–O1	263.8(4)	Sr2–O6	260.1(6)	Sr3–O5a	274.3(3)	K–O6b	299.5(1)
Sr1–O3a	267.6(3)	Sr2–O3b	261.2(3)	Sr3–O5b	274.3(3)	K–O5a	306.0(3)
Sr1–O3b	267.6(3)	Sr2–O4b	264.8(3)	Sr3–O2a	292.8(2)	K–O5b	306.0(3)
				Sr3–O2b	292.8(2)	K–O4a	338.8(3)
						K–O4b	338.8(3)
						K–O4c	361.4(3)
						K–O4d	361.4(3)
$\varnothing$ Sr1–O	260.0	$\varnothing$ Sr2–O	258.6	$\varnothing$ Sr3–O	270.1	$\varnothing$ K–O	314.3
B1–O2	136.2(7)	B2–O1	137.8(7)	B3–O6	136.7(7)		
B1–O3a	140.6(4)	B2–O5a	139.8(4)	B3–O4a	138.7(4)		
B1–O3b	140.6(4)	B2–O5b	139.8(4)	B3–O4b	138.7(4)		
$\varnothing$ B1–O	139.1	$\varnothing$ B2–O	139.1	$\varnothing$ B3–O	138.0	$\varnothing$ B–O	138.7

Table 5. Interatomic distances (pm) in  $\text{KSr}_4(\text{BO}_3)_3$  (space group: *Ama2*) calculated with the single-crystal lattice parameters (standard deviations in parentheses).

O2–B1–O3	121.6(2)	O1–B2–O5	121.1(2)	O6–B3–O4	120.0(2)
O2–B1–O3	121.6(2)	O1–B2–O5	121.1(2)	O6–B3–O4	120.0(2)
O3–B1–O3	116.7(5)	O5–B2–O5	117.7(4)	O4–B3–O4	120.0(5)
$\varnothing$ O–B1–O	120.0	$\varnothing$ O–B2–O	120.0	$\varnothing$ O–B3–O	120.0

Table 6. Interatomic angles (deg) in  $\text{KSr}_4(\text{BO}_3)_3$  (space group: *Ama2*) calculated with the single-crystal lattice parameters (standard deviations in parentheses).

pared to the data given by Wu *et al.* [1], which reveal unusual low and high B–O distances from 130(2) to 144 (2) pm with an average value of 139 pm and angles from 111.8(1) to 123.9(2)°, the values from the single-crystal refinement are much more reasonable.

Compared to the powder data [1], the coordination number of the potassium ions is extended from 8 to 8+4, as MAPLE calculations (*Madelung Part of Lattice Energy*) [15–17] have revealed. The K–O distances (Table 5) of the inner coordination sphere are distributed between 286.7(3) and 306.0(3) pm, leading to EcoN values between 1.29 and 0.90. The outer coordination sphere starts at 338.8(3) pm and ends at 361.4(3) pm with EcoN values between 0.37 and 0.14. The coordination number of the strontium ions remains unchanged. Sr1 and Sr2 are eightfold coordinated with

Sr–O distances from 255.6(3) to 267.6 pm and from 251.5(3) to 264.8(3) pm, respectively. Both are contained in a distorted bicapped trigonal prism. Sr3 is coordinated by nine oxygen atoms at distances between 255.1(4) and 292.8(2) pm. The coordination polyhedron is a distorted tricapped trigonal prism. The coordination spheres of the alkali and earth alkaline cations are shown in Fig. 3.

The bond-valence sums of the individual cations and anions of  $\text{KSr}_4(\text{BO}_3)_3$  were calculated from the crystal structure using the bond-length/bond-strength ( $\Sigma V$ ) [18, 19] and the CHARDI concept (*Charge Distribution in Solids,  $\Sigma Q$* ) [20, 21]. The values of both calculations are shown in Table 7.

A comparison of the MAPLE value [15–17] of  $\text{KSr}_4(\text{BO}_3)_3$  with the MAPLE value received from

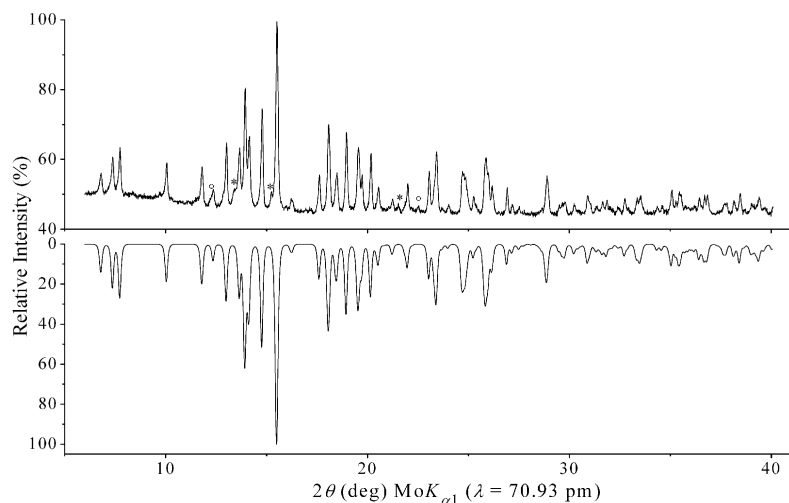


Fig. 1. Experimental powder pattern of  $\text{KSr}_4(\text{BO}_3)_3$  (top), compared with the theoretical powder pattern (bottom) simulated from single-crystal data. Additional reflections in the measured pattern caused by hexagonal BN from the crucible are marked with a ring. Unidentified reflections are marked with an asterisk.

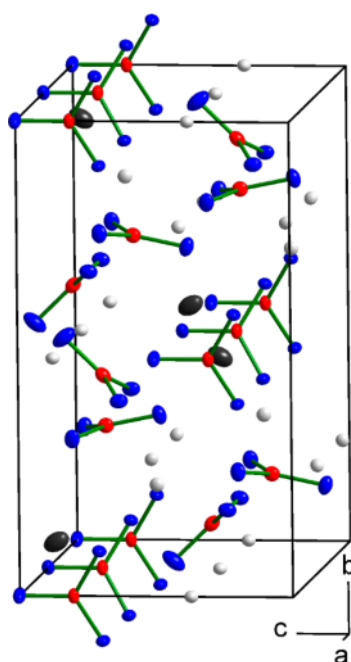


Fig. 2 (color online). Projection of the crystal structure of  $\text{KSr}_4(\text{BO}_3)_3$  with  $\text{BO}_3$  groups, potassium cations (dark spheres) and strontium cations (light spheres). Spheres: 70 % probability ellipsoids.

the summation of the binary components  $\gamma\text{-K}_2\text{O}$  [22],  $\text{SrO}$  [23] and the high-pressure modification  $\text{B}_2\text{O}_3\text{-II}$  [24] gave a value of  $49\,532\text{ kJ mol}^{-1}$  for  $\text{KSr}_4(\text{BO}_3)_3$  in comparison to  $49\,296\text{ kJ mol}^{-1}$  for the summation of the components (deviation = 0.5 % or  $236\text{ kJ mol}^{-1}$ ). The deviation lies within the accuracy of the method.

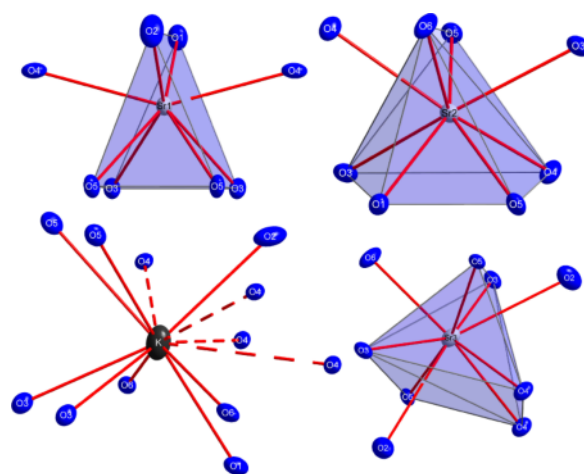


Fig. 3 (color online). Coordination spheres of the K and Sr cations (red lines) with the prisms of the coordination polyhedra around the Sr cations (blue).

#### Vibrational spectroscopy

The single-crystal FTIR-ATR and the single-crystal Raman spectra of  $\text{KSr}_4(\text{BO}_3)_3$  are shown in Figs. 4 and 5, respectively. The FTIR-ATR spectrum shows bands and shoulders at  $781$ ,  $835$ ,  $1132$ ,  $1246$ ,  $1340$ ,  $1591$ , and  $1662\text{ cm}^{-1}$ . Smaller bands and shoulders are found at  $615$ ,  $658$ ,  $669$ ,  $684$ ,  $739$ ,  $1027$ ,  $1062$ ,  $1174$ ,  $1290$ ,  $1373$ , and  $1437\text{ cm}^{-1}$ . The Raman spectrum contains strong peaks at  $80$ ,  $141$ ,  $294$ ,  $609$ ,  $899$ , and  $912\text{ cm}^{-1}$ , while weaker peaks and shoulders are found at  $95$ ,  $124$ ,  $133$ ,  $150$ ,  $166$ ,  $178$ ,  $226$ ,  $242$ ,  $273$ ,  $571$ ,  $600$ ,  $615$ ,  $622$ ,  $628$ ,  $888$ , and  $1238\text{ cm}^{-1}$ .

Table 7. Charge distribution in  $\text{KSr}_4(\text{BO}_3)_3$ , calculated with the bond-length/bond-strength ( $\Sigma V$ ) and the CHARDI ( $\Sigma Q$ ) concept.

	K	Sr1	Sr2	Sr3	B1	B2	B3
$\Sigma V$	1.00	2.01	1.97	1.99	3.15	2.96	2.94
$\Sigma Q$	1.06	2.20	2.27	1.99	2.84	2.84	2.93
	O1	O2	O3	O4	O5	O6	
$\Sigma V$	-1.93	-1.73	-2.03	-2.03	-2.09	-2.05	
$\Sigma Q$	-1.94	-1.65	-2.08	-2.11	-2.14	-2.06	

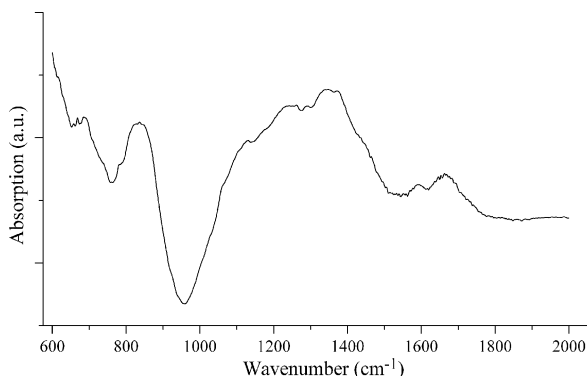


Fig. 4. Single-crystal ATR-FT-IR spectrum of  $\text{KSr}_4(\text{BO}_3)_3$ .

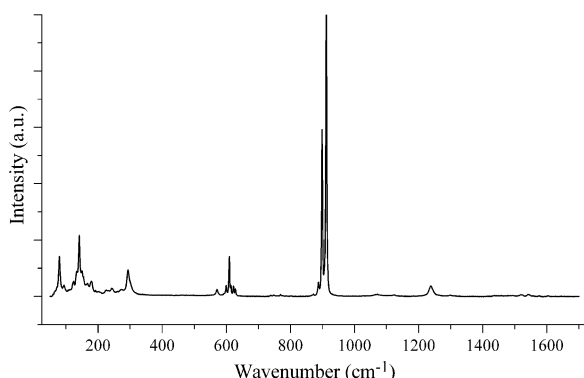


Fig. 5. Single-crystal Raman spectrum of  $\text{KSr}_4(\text{BO}_3)_3$ .

For borates in general, bands in the region of  $800\text{--}1100\text{ cm}^{-1}$  usually apply to stretching modes

of boron atoms which are tetrahedrally coordinated to oxygen atoms [25, 26], while absorption bands at  $1200\text{--}1450\text{ cm}^{-1}$  are expected for borates containing  $\text{BO}_3$  groups [26, 27]. This fits well to the findings in the FTIR-ATR spectrum, where the bands above  $1100\text{ cm}^{-1}$  can be assigned to the B–O stretching modes of planar  $\text{BO}_3$  groups, while bands at  $700\text{--}800\text{ cm}^{-1}$  can be assigned to out of plane bending vibrations as suggested by Wu *et al.* [1]. The Raman spectrum indicates strong peaks at  $900\text{ cm}^{-1}$ , which were also observed in other phases like  $\text{Pr}_4\text{B}_3\text{O}_{10}\text{F}$  [28] and  $\text{RE}_5(\text{BO}_3)_2\text{F}_9$  ( $\text{RE} = \text{Er}, \text{Yb}$ ) [29], and in hydrated monoborates [30]. They are assigned to symmetric stretching vibrations of the isolated  $\text{BO}_3$  groups [30]. Furthermore, a weak absorption could be detected in the range of  $3000\text{ to }3600\text{ cm}^{-1}$  that arises presumably from surface water.

## Conclusion

Single crystals of  $\text{KSr}_4(\text{BO}_3)_3$  were synthesized under high-pressure conditions of 3 GPa and  $1300^\circ\text{C}$ . The powder data refinement of Wu *et al.* [1] could be supplemented by more accurate data, containing a more precise set of atomic coordinates including anisotropic displacement parameters. This set of coordinates leads to more reasonable interatomic distances and angles. To add spectroscopic data for this compound, single-crystal FTIR-ATR and Raman measurements were performed. The single-crystal FTIR-ATR spectrum matches well with the powder IR data presented by Wu *et al.* The Raman spectrum is typical for a compound containing solely isolated  $\text{BO}_3$  groups

## Acknowledgement

The authors would like to thank L. Perfler (University of Innsbruck) for the Raman spectroscopic measurements, Dr. G. Heymann for recording the single-crystal data set and Univ.-Prof. Dr. R. Stalder (University of Innsbruck) for the usage of the FTIR-ATR spectrometer.

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