Ivlev, S.; Kraus, F.; Karttunen, A.J.; Ostvald, R.Z.

**RbBrF₄ Revisited**

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RbBrF₄ revisited

Sergei Ivlev,*[a,b] Antti Karttunen,[c] Roman Ostvald,[b] and Florian Kraus*[a]

Keywords: Tetrafluoridobromate; Rubidium; Powder X-ray diffraction; Crystal Structure; DFT

Rubidium tetrafluoridobromate(III) was synthesized and structurally characterized. The compound is isotypic to sodium and potassium tetrafluoridobromate(III), and crystallizes in the tetragonal space group I4/mcm (dI24, KBrF₄ structure type) with a = 6.3718(2), c = 11.4934(3) Å, V = 466.63(2) Å³, Z = 4, at T = 293 K. Additionally we investigated the compound by means of IR- and Raman spectroscopy as well as theoretical investigations. The data obtained by quantum chemical calculations confirm the crystal structure, and also the atomic distances and angles with an average deviation of 2.2 to 2.7%.

Results and Discussion

Synthesis of RbBrF₄

Rubidium tetrafluoridobromate(III) is obtained by the following, idealized but plausible, reaction equation 1:

$$6 \text{RbCl} + 8 \text{BrF}_3 \rightarrow 6 \text{RbBrF}_4 + \text{Br}_2 + 3 \text{Cl}_2$$

Equation 1

The reaction is carried out in a PTFE test tube with the addition of a protective layer of Freon-113, which is inert to the reactants as well as the products. Moreover, it acts as a heat absorber and thus prevents the evaporation of BrF₃. The details of this technique were reported in our previous works \cite{7,12,13} and elsewhere \cite{2,10}.

In order to prevent the formation of rubidium heptafluoridobromide(III), RbBF₃\(\text{F}_7\) (which is possible due to the formation of regions with a local excess of liquid BrF₃, similarly to the case of CsBF₃\(\text{F}_7\))\cite{12}, a small excess of RbCl (3\% by mass of RbCl) is used. The synthesized solid product appears as a white crystalline powder, which slowly hydrolyzes on moist air releasing bromine vapors, HF, and presumably O₂.

According to quantitative X-ray fluorescence analysis using rubidium bromide as a standard, the mass ratio of Rb:Br in the product was equal to 1:1.22 due to the slight excess of Rb in the synthesis. This is equivalent to \(\approx 2.9\%\) (by mass of RbCl), and is in good agreement with the 3\% used in excess.

Powder X-Ray Diffraction Study on RbBrF₄

The powder X-ray diffraction pattern of the sample measured at 293 K is shown in Figure 1.

Introduction

Alkali and alkaline earth metal tetrafluoridobromates(III), M⁺⁺⁺(BrF₄)₄, may be perspective fluorinating agents in various fields of chemistry and chemical technology. Recent studies \cite{1-7} showed for example their potential use for the recycling of noble metals, the so-called "urban mining". The exceptional oxidative and fluorinating ability of the tetrafluoridobromates(III) allows even the conversion of the most inert noble as well as refractory metals into compounds for further "classical" extraction and separation procedures.

It is interesting to note that the physical and chemical properties of some tetrafluoridobromates(III) are still not fully established, whereas some others, mainly KBrF₄ and BaBrF₃O₂ are well documented.\cite{8-14} The single crystal structures of KBrF₄ \cite{15-17}, RbBrF₄ \cite{8}, and CsBrF₃ \cite{12} have been determined. Single crystal structures are not only of purely theoretical interest but are a precondition to obtain technologically important parameters by computer simulations, such as the values of thermodynamic functions (enthalpy of formation, entropy, heat capacity, etc.) at given temperatures, or to assess the stability, solubility and reactivity of the compounds. It was reported for RbBrF₄ that the rubidium atoms occupy the special position 4c (0; 0; 0) of the space group I4/mcm.\cite{18,19} This leads to a square prismatic coordination of the Rb atoms, which is in contrast to the K⁺ coordination of KBrF₄. There, the cations reside on the special position 4a (0; 0; ¼), thus a square antiprismatic coordination is obtained.\cite{15-19} As rubidium salts are often isotypic to the respective potassium salts, we reinvestigated the crystal structure of RbBrF₄.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/zaac.201000xxx or from the author. ((Please delete if not appropriate.))
Despite the presence of some unreacted RbCl, as indicated by the reflections of small intensities, there are no
significant reflection overlaps, which make the powder
pattern easily suitable for Rietveld refinement.

The obtained diffraction pattern can be indexed in the
tetragonal crystal family with the lattice parameters $a =
6.3718(2)$, $c = 11.4934(3)$ Å, $V = 466.63(2)$ Å$^3$. The
observed reflection extinction conditions pointed to a body-
centered lattice and the manual analysis of the extinction
conditions narrowed the possible choice of space groups
down to $I4cm$ (No. 108), $I4$ $c2$ (No. 120) and $I4/mcm$ (No.
140). Since the RbBrF$_4$ crystal structure is not expected to
be non-centrosymmetric and also taking the structures of
NaBrF$_3$ and KBrF$_3$ into account, the Rietveld refinement of
rubidium tetrafluoridobromate(III) was performed in the
space group $I4/mcm$ (No. 140). Additionally, structure
solutions using the SUPERFLIP algorithm [20] yielded the
same space group. It should be noted that the obtained cell
parameters are in good agreement with the ones published in
[8]. Further details of the attempted refinement in the other
two space groups are given in the Supporting Information.

The measured pycnometric density of RbBrF$_4$ is $3.33 \pm 0.01$
g/cm$^3$, and thus $Z$ is equal to 4.

The value of the crystallographic density is $3.43 \text{ g/cm}^3$,
which fits nicely to the experimentally determined value.
Moreover, if the mass ratio of RbBrF$_4$:RbCl is calculated
using the Rietveld method (96.5% : 3.5%), the theoretical
density for the mixture would be $3.40 \text{ g/cm}^3$, which is even
closer to the experimentally observed value.

The crystallographic details for RbBrF$_4$ are shown in
Table 1.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
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<tr>
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</tr>
<tr>
<td>Molar mass, g/mol</td>
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</tr>
<tr>
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</tr>
<tr>
<td>Space group</td>
<td>$I4/mcm$</td>
</tr>
<tr>
<td>$a$, Å</td>
<td>6.3718(2)</td>
</tr>
<tr>
<td>$c$, Å</td>
<td>11.4934(3)</td>
</tr>
<tr>
<td>$V$, Å$^3$</td>
<td>466.63(2)</td>
</tr>
<tr>
<td>$Z$</td>
<td>4</td>
</tr>
<tr>
<td>$\rho_{exp}$, g/cm$^3$</td>
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</tr>
<tr>
<td>$\rho_{Rietveld}$, g/cm$^3$</td>
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<tr>
<td>$\rho_{calc}$, g/cm$^3$</td>
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<tr>
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<tr>
<td>$T$, K</td>
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<tr>
<td>$Rp$, $wRp$</td>
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<tr>
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</tr>
<tr>
<td>No. of data points, parameters, constraints, restraints</td>
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</tr>
<tr>
<td>2θ range measured (min; max; increment)</td>
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</tr>
<tr>
<td>2θ range refined (min; max; increment)</td>
<td>10.000; 69.610; 0.015</td>
</tr>
</tbody>
</table>

**Crystal Structure of RbBrF$_4$**

The structure solution was carried out manually and also
using the SUPERFLIP algorithm implemented in Jana2006
[20], the structure refinement was carried out with the
Jana2006 software [21]. A section of the structure is shown in
Figure 2, and the crystal structure in Figure 3.

The measured pycnometric density of RbBrF$_4$ is $3.33 \pm 0.01$
g/cm$^3$, and thus $Z$ is equal to 4.

The value of the crystallographic density is $3.43 \text{ g/cm}^3$,
which fits nicely to the experimentally determined value.
Moreover, if the mass ratio of RbBrF$_4$:RbCl is calculated
using the Rietveld method (96.5% : 3.5%), the theoretical
density for the mixture would be $3.40 \text{ g/cm}^3$, which is even
closer to the experimentally observed value.

The crystallographic details for RbBrF$_4$ are shown in
Table 1.
The rubidium atoms occupy the Wyckoff position 4a, and the square planar BrF$_4^-$ anions with their bromine atoms the Wyckoff position 4d. This arrangement makes the structure chemically more plausible and isotopic to KBrF$_4$ of which the structure was previously well-characterized using also neutron diffraction [15].

The location of the Rb atoms on the special position 4a leads to a square-antiprismatic coordination by F-atoms, with Rb–F distances of 2.851(7) Å. This value nicely agrees to the Rb–F distance observed in the isotypic compound RbAuF$_4$ with 2.85(2) Å. Square (sometimes distorted) prismatic coordination spheres of Rb atoms are frequent, e.g. as observed in the compounds RbBiF$_4$, RbAlF$_4$, RbFeF$_4$, with mean Rb–F distances of 2.3846, 2.918(1), and 2.98(1) Å, respectively. The experimentally determined Br–F distance in the title compound is 1.932(8) Å, which is very close to the values observed for KBrF$_4$ with 1.89(1) Å [15], for CsBrF$_4$ with 1.94(4) to 1.97(4) Å [12], for CsBr$_3$F$_7$ with 1.7686(11) to 2.1431(12) Å [12], for Ba(TiF$_4$)$_2$ with 1.801(4) to 1.935(2) Å [13], and also to the bond lengths observed for BrF$_4^-$ molecules in the gas phase with 1.721 to 1.810 Å (no s.u. given) [22,23] and the BrF$_3$ molecules in their crystal structure with 1.71(1) to 1.888(9) Å [24], as well as to the theoretically predicted Br–F distance in the isolated BrF$_4^-$ anion (1.8994 Å) [25].

If we carry out the refinement using the "old" model of the crystal structure on our powder pattern (with the Rb atom on the 4c position) the Rietveld refinement produces very bad agreement factors: $R_p = 0.4527$, $wR_p = 0.5848$, $R$(obs) = 0.6004, $wR^2$(obs) = 0.5580, $R$(all) = 0.6522, $wR^2$(all) = 0.5669. Additionally, the accuracy of the lattice parameters is one order of magnitude less with $a = 6.372(2)$, $c = 11.497(7)$ Å, $V = 466.68(4)$ Å$^3$, and for example in the BrF$_4^-$ anion the atomic distances are to long with 2.1031(8) Å and its angles are 100.727(12) and 79.273(7)$^\circ$. Furthermore, the isotropic displacement parameters of the Rb and Br atoms refined to negative values. Therefore the structure model with the Rb atom on the 4a position is clearly preferred over the "old" model.

**Computational Study**

In order to have a deeper insight into the structure of RbBrF$_4$, we carried out a full structural optimization of the cell parameters and atomic positions of the previously reported and the crystal structure described here. The optimization was done within space group $Ih4/mcm$ and the DFT-PBE0/SVP level of theory (see Experimental Section for Computational Details). The cell parameters as well as the selected bond distances and angles for both structures are shown in Table 2. Optimized and experimentally observed atom positions for both structures are given in Table S1 and Table S2 (Supporting Information).

According to the obtained results the interatomic distances of both structures are comparable with those observed in other tetrafluoridobromates(III) [10,12,13,15]. However, the bond angles of the BrF$_4^-$ anion of the previously reported structure show a strong distortion from the expected square-planar arrangement. Moreover, the calculated cell parameters deviate by 9.3% (for $a$) and 22.3% (for $c$) from the experimentally determined values, whereas the structure described here shows a nice correlation between theory and experiment with an average difference of ~2.5%. These facts additionally indicate that the rubidium atoms occupy the special position 4a inside the lattice of RbBrF$_4$.

**Vibrational spectroscopy**

After conducting a full geometry optimization the IR- and Raman spectra for both optimized structures were calculated and are shown in Figure 4.

The calculated spectra for the structures determined here and in [8] appeared to be very similar to each other, which may be expected since the spectra are mostly determined by the chemical bonding inside the BrF$_4^-$ anions. But in spite of that there are clearer differences in the lower wavenumbers due to the differences in the overall structures. Therefore, we carried out the experimental measurements of the IR- and Raman spectra of RbBrF$_4$ (Figure 5).

The Raman spectrum shows a good correlation of the wavenumbers and the relative intensities with the calculated one, although, the band positions are slightly shifted (see the Supporting information for detailed analysis of the Raman spectrum). The theoretically calculated Raman spectrum for the RbBrF$_4$ structure with the Rb atom on the 4c Wyckoff position [8] shows clear differences with respect to the experimentally observed spectrum: an additional band at 282 cm$^{-1}$, no band corresponding to the experimentally observed band at 241 cm$^{-1}$, and poor agreement with the
experimentally observed band features at around 100 cm\(^{-1}\). In summary, the predicted Raman spectrum supports the revised structure with the Rb atom on the 4a Wyckoff position.

![Graph 1: Experimental Raman vs. Theoretical Raman spectra](image1)

Figure 4. The theoretically predicted vibrational spectra of RbBrF\(_4\).

The features of the IR spectrum are also in sufficient correspondence with the results of the \textit{ab initio} calculations, although the sample-dependent shapes of the bands could not be predicted (see Supporting information for detailed analysis of the IR spectrum). The sharp extra band at 177 cm\(^{-1}\) can be attributed to RbCl which is intentionally present (see Supporting information). Since the theoretical IR peak positions are rather similar for both crystal structures and the predicted intensities are in both cases so different from the experiment, the theoretical IR spectra are not as useful for differentiating the two crystal structures as the Raman spectra.

![Graph 2: Experimental IR vs. Theoretical IR spectra](image2)

Conclusions

Polycrystalline samples of rubidium tetrafluoridobromate(III) RbBrF\(_4\) were directly synthesized from RbCl and BrF\(_3\). The compound crystallizes in the tetragonal space group \textit{I}4/\textit{mcm} with \(a = 6.3718(2)\), \(c = 11.4934(3)\) Å, \(V = 466.63(2)\) Å\(^3\), and \(Z = 4\) at 293 K. The cell parameters are in a good correspondence with the ones published previously \cite{8}. However, the elucidated crystal structure is different in terms of the Rb atom position. We observe the occupation of the 4a Wyckoff position in contrast to the previously reported occupation of the 4c position. This finding is supported by the additional theoretical and IR/Raman spectroscopic investigations. Also, the crystal structure of RbBrF\(_4\) reported here is isotypic to the well-characterized potassium tetrafluoridobromate(III) KBrF\(_4\).

![Graph 3: Measured Raman spectra vs. Theoretical Raman spectra](image3)

Figure 5. Measured Raman (top) and IR (bottom) spectra of RbBrF\(_4\).

Experimental Section

General: All operations with RbBrF\(_4\) were carried out in an atmosphere of dry and purified argon (Westfalen AG, Germany), so that a possible contact of the substances with moisture or air was minimized (O\(_2\) < 1 ppm, H\(_2\)O < 1 ppm). RbCl (“chemically pure” grade, JSC Vekton, Russia) was used without further purification. BrF\(_3\) was synthesized by slowly passing gaseous fluorine through liquid bromine in a nickel reactor with continuous cooling \cite{26,27}. After completion of the reaction, BrF\(_3\) was distilled, and only the fraction with b.p. = 125 °C was used for the experiments. Then, RbCl and BrF\(_3\) were used for the preparation of RbBrF\(_4\).

Preparation of RbBrF\(_4\): RbCl (2.71 g, 22.5 mmol, 1.03 equiv.) with an excess of 0.7 mmol (3% by mass) was placed in a PTFE
tube and layered with Freon-113 (15 mL). Liquid BrF₃ (3.99 g, 29.1 mmol, 1.00 equiv.) was added dropwise under vigorous stirring. More portions of Freon-113 were added as needed. The total yield of dry product was 5.26 g (consisting of 0.18 g RbCl (1.5 mmol) and 5.08 g RbBrF₃ (21.1 mmol, 96.5% of theory) – an estimation calculated using the Rietveld method. More details of the quantitative analysis of the product are given in the Results and Discussion section.

**X-ray Fluorescence Analysis:** The energy dispersive X-ray fluorescence analysis (EDXRF) was carried out with an ARL QUANT’X spectrometer (Thermo Scientific, USA) equipped with a Peltier-cooled Si(Li) detector. The measurements were done under the most suitable experimental conditions in order to obtain the primary lines for both rubidium and bromine: a thick Pd filter with a voltage of 28 kV on the X-ray tube. The duration of one measurement was equal to 120 s of lifetime. All measurements were done in air with the samples introduced in the form of aqueous solutions after the hydrolysis of RbBrF₃. The Raman range of 4000 cm⁻¹ to 200 cm⁻¹ was recorded using a Bruker IFS 113v (Karlsruhe, Germany) FTIR spectrometer under an Ar atmosphere. The Raman intensities were obtained by using the computational schemes implemented in CRYSTAL.

**Discussion** (see footnote on the first page of this article): The optimized and experimentally determined atom positions for RbBrF₃, the full-range IR spectrum and additional computational details.

**Acknowledgement**

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**Supporting Information**

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